SPECTROSCOPIC, KINETIC, AND SYNTHETIC STUDIES
ON SOME OF THE FIRST ROW TRANSITION METAL
HALOCARBONYLS AND THEIR DERIVATIVES

Ph.D.

Hagop Krikor Spendjian

Chemistry
Department

ABSTRACT

The solid-state infrared and Raman spectra of the complexes $Mn(CO)_5X$ (X =Cl, Br, I) were recorded and a vibrational assignment proposed. The spectra of $[Mn(CO)_4X]_2$ (X = Br, I) were also recorded.

The isotopic CO exchange reactions of the complexes *cis*-$Fe(CO)_4X_2$ (X = Br, I) and *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$) were investigated. The CO stretching frequencies were assigned and Cotton-Kraihanzel parameters calculated. The exchange stereochemistries were studied.

The reactions of $Mn(CO)_5X$ (X = Cl, Br) with monodentate phosphites were found to give complexes of the type *cis*-$Mn(CO)_2L_3X$. The latter reacted with diphos and triphos (A-A) to give *cis*-$Mn(CO)_2L(A\text{-}A)X$. The complexes *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ (X = Cl, Br) reacted with the bidentate ligands, diphos, diars, diarsine, and dipy, to yield *cis*-$Mn(CO)_3(A\text{-}A)X$ and *cis*-$Mn(CO)_2L(A\text{-}A)X$. $Mn(CO)_5X$ reacted with triphos to give *cis*-$Mn(CO)_3$(triphos)X in which the ligand behaved as a bidentate. *cis*-$Mn(CO)_3$(triphos)Br reacted with another molecule of $Mn(CO)_5Br$ to give a bridged complex, $BrMn(CO)_3$(triphos)$Mn(CO)_4Br$.

The thermal decomposition of the *trans*-$Mn(CO)_3(PPh_3)_2X$ (X = Cl, Br, I) species to *cis*-$Mn(CO)_4(PPh_3)X$ was examined kinetically and found to follow a first-order rate law. The reactions of *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$) with bidentate ligands to give *cis*-$Mn(CO)_3(A\text{-}A)Br$ were also examined. The rates were found to depend both on the nature and on the concentration of the entering ligand. Possible mechanisms were suggested.

Transition Metal Halocarbonyls and their Derivatives

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Hagop Krikor Spendjian

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To my parents

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LIST OF ABBREVIATIONS

Me - methyl

Et - ethyl

Bu - butyl

Ph - phenyl

Cp - cyclopentadienyl

py - pyridine

γ-pic - γ-picoline

o-phen - *o*-phenanthroline

dipy - 2,2′-dipyridyl

diars - *o*-phenylenebisdimethylarsine

diphos - 1,2-bis(diphenylphosphino)ethane

diarsine - 1,2-bis(diphenylarsino)ethane

triphos - bis(2-diphenylphosphino)phenylphosphine

disulph - 1,2-bisphenylthioethane

dien - ethylenediamine

Tdp - trisdimethylaminophosphine

TMED - tetramethylethylenediamine

dithia - 2,5-dithiahexane

s-TCE - *s*-tetrachloroethane

THF - tetrahydrofuran

diglyme - 2-methoxyethylether

L - a monodentate ligand

X - a halogen

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PREFACE

The author would like to acquaint the reader with the work described in this dissertation. For this purpose, a short review is presented below.

The low-frequency infrared and Raman spectra of the complexes $Mn(CO)_5X$ (X = Cl, Br, I) have been recorded and a vibrational assignment proposed. In the course of the investigation the solid-state infrared and Raman spectra of the complexes $[Mn(CO)_4X]_2$ (X = Br, I) were also recorded. These assignments were to be used for performing rigorous normal coordinate calculations which would shed some light onto the bonding properties of these complexes. However, while the results of this work were being prepared for publication other reports on the vibrational assignment of these and similar complexes appeared in the literature. It was therefore decided not to proceed with the force constant calculations mentioned above. (The results of the spectroscopic investigation on the $Mn(CO)_5X$ system are reported and discussed in Part I of the thesis.)

Following this, it was decided to use the recently reported technique of isotopic CO exchange as a tool in the infrared spectroscopic investigation of some metal carbonyl complexes. Two systems were studied. The first was that of the *cis*-$Fe(CO)_4X_2$ (X = Br, I) complexes, the second that of the *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$) complexes. For both systems the fundamental CO stretching frequencies of the all-^{12}CO and the isotopically substituted molecules were assigned and Cotton-Kraihanzel force constant parameters calculated. It was also possible to come to some conclusion concerning stereospecific substitution in these complexes. (These results are reported and discussed in Part II.)

The CO exchange reaction with *trans*-$Mn(CO)_3L_2Br$ indicated that both the *trans*-CO groups and the ligands L were labile. This led to a study of the reactions of complexes of this type with bidentate ligands. A number of new dicarbonyl complexes of the type *cis*-$Mn(CO)_2$-L(bidentate)X were prepared in this way. The reactions of $Mn(CO)_5Br$ with tertiary phosphites were also examined and found to give products of the type *cis*-$Mn(CO)_2L_3X$. Some reactions of $Mn(CO)_5X$ and its derivatives with a potentially tridentate ligand, triphos, were also studied. (The results of these synthetic studies are reported in Part III.)

The complexes *trans*-$Mn(CO)_3(PPh_3)_2X$ were found to decompose thermally to give *cis*-$Mn(CO)_4(PPh_3)Br$. Also, the complexes *cis*-$Mn(CO)_4LBr$ reacted with bidentates to give *cis*-$Mn(CO)_3$(bidentate)Br. The kinetics of these reactions were investigated and possible reaction mechanisms proposed. (Part IV.)

SOURCES OF MATERIALS

Compound	Source
$Fe(CO)_5$	Alfa Inorganics
$Mn_2(CO)_{10}$	"
PPh_3	"
$AsPh_3$	Aldrich Chemicals Co. Inc.
$SbPh_3$	"
$P(OPh)_3$	"
$P(OMe)_3$	"
$P(OEt)_3$	"
$P(OCH{:}CHCH_3)_3$	"
diphos	"
diars	"
diarsine	"
Br_2	"
I_2	"
py	Fisher Scientific Co.
dipy	"
triphos	Strem Chemicals Inc.
Cl_2	Matheson of Canada Ltd.
CO	"
^{13}CO	Merck, Sharp, and Dohme Ltd., Montreal, Canada
$C^{18}O$	Miles Laboratories Inc., Elkhart, Indiana
chloroform	A & C American Chemicals
n-hexane	"
carbon disulphide	Fisher Scientific Co.
cyclohexane	"
s-tetrachlorethane	"
benzene	Anachemia Chemicals Ltd.
petroleum ether	"
tetrahydrofuran	Aldrich Chemicals Co. Inc.
diglyme	"

PART I

VIBRATIONAL SPECTRA OF HALOCARBONYLMANGANESE(I) DERIVATIVES

CHAPTER I INTRODUCTION

Although a wealth of infrared spectroscopic data have been gathered for metal carbonyl complexes of all types,[1] the great majority of investigations has been confined to the carbonyl stretching region between 2200-1800cm^{-1}, with little attention being paid to other regions of the spectra. Apart from the carbonyl stretching modes ν(CO), one would expect to observe metal-carbon stretching modes, ν(MC), between 560-360cm^{-1}, linear metal-carbon-oxygen bending modes, δ(MCO), between 790-300cm^{-1}, and carbon-metal-carbon bending modes, δ(CMC), below 150cm^{-1}. Recently,there has been particular interest in the low-frequency regions. These studies have proved useful, as a means of structure determination or clarification, in normal coordinate analyses, and in the elucidation of the bonding properties of metal carbonyl complexes.

One of the main problems encountered in attempting to assign ν(MC) and δ(MCO) vibrations in metal carbonyls is that since both types of vibration occur at similar frequencies there is extensive mixing of bending and stretching modes of the same symmetry type, such that a ν(MC) mode may be only "essentially" a stretching vibration, etc.[2] The earliest indication as to whether any specific frequency ranges could be designated to facilitate vibrational assignments, was provided by the force constant calculations on the Group VIB metal hexacarbonyls performed by Murata and Kawai[3] and by Jones.[4] These workers found that in these cases at least, all the ν(MC) vibrations lie below the δ(MCO) vibrations. These results are shown in the following table.

TABLE I. FIRST ASSIGNMENTS OF ν(MC) AND δ(MCO) MODES IN THE VAPOUR PHASE SPECTRA OF THE GROUP VIB HEXACARBONYLS.[3,4] (cm^{-1})

	ν(MC)			δ(MCO)			
	$\underline{a}_{1g}$	$\underline{e}_{g}$	$\underline{t}_{1u}$	$\underline{t}_{1g}$	$\underline{t}_{2g}$	$\underline{t}_{1u}$	$\underline{t}_{2u}$
$Cr(CO)_6$	390	363	441	534	562	668	512
$Mo(CO)_6$	392	344	368	481	506	593	512
$W(CO)_6$	420	363	374	484	509	585	520

Poilblanc and Bigorgne[5] came to a similar conclusion *via* a comparative study of the derivatives $M(CO)_{6-n}L_n$ (M = Mo and sometimes Cr or W;L = tertiary phosphines), when they found that the derivatives *trans*-$Mo(CO)_4[PEt_3]_2$ and *trans*-$Mo(CO)_4[P(OMe)_3]_2$ exhibited one infrared absorption near 400cm^{-1} and two infrared absorptions in the 600cm^{-1} region. The first absorption since it was unique, was attributed to the doubly degenerate ν(MC) stretch $\underline{e}_u$, while the latter conformed to the two expected i.r. active δ(MCO) modes ($\underline{a}_{2u}$ + $\underline{e}_u$) for *trans*-disubstituted complexes. The early Raman work of Stammreich *et al.*[6,7,8] pointed in the same direction. For example, polarized bands indicative of totally symmetric modes were observed for $Fe(CO)_5$ at 414cm^{-1},[6] for $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ at 439cm^{-1} and 464cm^{-1}, respectively,[7] and at 380cm^{-1} for $Ni(CO)_4$.[8] Since totally symmetric modes for these complexes are expected for ν(MC) and not for δ(MCO) modes, they were all assigned to the former, and all the ν(MC) modes were considered to be at lower frequencies than the δ(MCO) modes. Stammreich *et al.*[7] made the general statement that,

> "A comparative study of all available Raman data on metal carbonyl compounds leads to the purely qualitative conclusion that the shift corresponding to M-(CO) stretching motions appear at higher intensities and lower frequencies than those of the M-C-O bending modes".

Jones,[9] and Bigorgne and co-workers,[10-12] had also used Raman data to reach similar conclusions for $Ni(CO)_4$; and Bigorgne and co-workers also came to this assignment in studies of $Ni(CO)_3AsEt_3$[13] and $Ni(CO)_{4-n}(PF_3)_n$ (n = 1,2,3).[14] Adams studied the infrared spectra of fifty-two metal carbonyl complexes and assigned all the bands observed in the range 682-468cm^{-1} to carbonyl bending modes.[15]

The most widely used methods for assigning the ν(MC) and δ(MC) modes are obviously the same as those used for ν(CO), *viz.* number and relative position of bands, relative intensity, comparison between infrared and Raman data, force constant calculations, and prediction of overtone and combination modes. However, because of problems such as the mixing of modes, unavailability of Raman data, or insufficient solubility of the complexes in some cases for the observation of all the predicted infrared and Raman bands certain additional aids must sometimes be used to be able to explain the data available.

One obvious and very useful method used in assigning the ν(MC) and δ(MCO) modes is the comparison of spectra of structurally related molecules. An interesting example of this is the assignment[16] of the modes of $Hg[Co(CO)_4]_2$ and $Hg[Co(CO)_3L]_2$ where L is a tertiary phosphine, phosphite, arsine or stibine. In going from the parent compound to the substituted complexes the bands associated with the axial carbonyl groups would be expected to disappear.

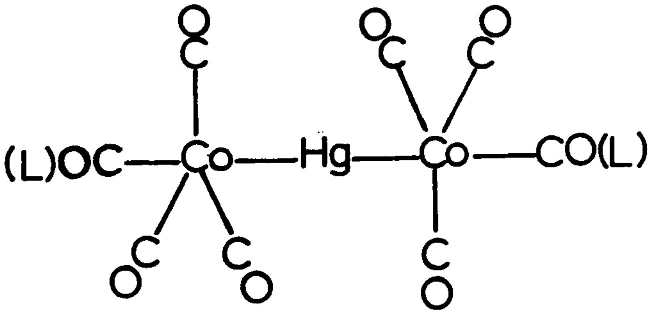

Figure 1.-Structure of $Hg[Co(CO)_4]_2$ and $Hg[Co(CO)_3L]_2$.

Furthermore, the fact that substitution of CO by weaker π-acceptor ligands would have a greater effect on certain bands than on others was used to assign the remaining modes. The frequencies of the similar molecules, $[LCo(CO)_3]_2$,were assigned in the same manner.[17]

In certain cases, the ν(MC) modes have been assigned by invoking the argument that, given the reciprocal nature of the M-C and C-O bond orders (following current bonding theories on metal carbonyls), they will be in an order opposite to that for the ν(CO) stretches. For example this method has been applied to $Os_3(CO)_{12}$[18] and to $Mn_2(CO)_{10}$ and $Mn_2(CO)_8L_2$ (L = tertiary phosphine or arsine).[19] In another study it was hoped that all the ν(MC) modes of $Mn(CO)_5L$ complexes could be identified by assuming a reciprocal relationship between the ν(MC) and ν(CO) modes, and that the characteristic intensity pattern of the ν(CO) modes would be reproduced for the ν(MC) vibrations.[20] However, these assumptions proved inadequate in this case to explain all the features of the spectra. This is not too unexpected since mixing of the weak ν(MC) modes with the comparatively strong δ(MCO) modes could confuse the expected intensity pattern.

A novel intensity argument has been proposed by Manning[21] who showed that the intensities of absorption bands due primarily to the δ(MCO) vibrations of $M(CO)_2$ groups could be explained if it was assumed that, when an M-C-O group was bent during a vibration, it would give rise to a dipole-gradient perpendicular to the M-C-O axis. Applying this principle to the various symmetry coordinates the bands of $(\pi\text{-}C_5H_5)Fe(CO)_2L$ ($L = PPh_3^+, I, SnCl_2I, SnPh_3$) and *trans*-$(\pi\text{-}C_5H_5)Mo(CO)_2(L)SnPh_3$ [$L = P(OMe)_3, PPh_3, SbPh_3$] have been assigned.

The last region of the spectrum of concern here is the region around $100cm^{-1}$. This region has been sparsely investigated owing to the unavailability of suitable instrumentation. In the early studies the bands occuring here were attributed to the C-M-C angle bending modes, δ(CMC). These initial studies were all reserved to Raman spectra, and it is only in the past few years that infrared data have made their appearance. The assignment of both infrared and Raman spectra in this region is severely complicated by the broadness of the bands, and in the case of solid state spectra by the appearance of lattice modes and their combinations.

In Chapter II of this part of the thesis a review will be given of the low-frequency (below $800cm^{-1}$) spectroscopic investigations performed on metal carbonyl complexes to date. The review will stress the various problems encountered in effecting low-frequency studies and in the assignment of the observed spectra, as well as the various means used to overcome these problems. The results of the author's investigation of the infrared and Raman spectra of some of the halocarbonylmanganese(I) derivatives will be presented in Chapter III. These results will be discussed and a vibrational assignment for the halopentacarbonylmanganese(I) complexes will be suggested.

CHAPTER II REVIEW OF LOW-FREQUENCY VIBRATIONAL STUDIES ON METAL CARBONYL COMPLEXES

A. BINARY METAL CARBONYLS

i. Tetrahedral - $Ni(CO)_4$

In 1961 Stammreich *et al.*[8] stated that "of all the vibrational spectra of metal carbonyl compounds, that of nickel carbonyl is by far the most thoroughly investigated." Since then many more studies on $Ni(CO)_4$ have been carried out making this statement equally true at the present time. The initial Raman measurements were carried out by Duncan and Murray,[22] and by Crawford and Horwitz,[23] while the infrared spectrum was first recorded by Crawford and Cross,[24] and Bailey and Gordon.[25] These studies were supplemented by the Raman work of Stammreich *et al.*[8] and of Bigorgne and his co-workers;[10,12,26,27] while Jones *et al.*[9,28-32] have provided the bulk of infrared data currently available.

For tetrahedral $Ni(CO)_4$, the following fundamental modes are expected: $2\underline{a}_1 + 2\underline{e} + 4\underline{t}_2 + \underline{t}_1$ which may be subdivided into $\nu(CO)$: $\underline{a}_1 + \underline{t}_2$, $\nu(MC)$: $\underline{a}_1 + \underline{t}_2$, $\delta(MCO)$: $\underline{e} + \underline{t}_2 + \underline{t}_1$, and $\delta(CMC)$: $\underline{e} + \underline{t}_2$. The $\underline{a}_1$ and $\underline{e}$ modes are Raman active, the $\underline{t}_2$ modes are both infrared and Raman active, while the $\underline{t}_1$ mode is inactive.

There has been no argument in the assignment of the $\underline{a}_1$ and $\underline{t}_2$ fundamentals since the former appear as very intense polarized lines in the Raman spectrum, and the latter are observed in both the infrared and the Raman spectra. The spectroscopically inactive $\underline{t}_1$ $\delta(MCO)$ mode of $\underline{t}_1$ has been satisfactorily assigned by a consideration of overtone and combination bands.[8,9,11] A band near 600cm^{-1} in the Raman spectrum was found to be polarized and, since no such band was expected in this region, it had therefore to arise from an overtone or combination mode which contained an $\underline{A}_1$ state.* The only possibility for this was $\underline{t}_1^{\,2}$ ($2\nu_9$, $\underline{A}_1 + \underline{E} + \underline{T}_2$). This assignment was later confirmed by the observation of a band at 303cm^{-1} in the spectrum of the solid,[32] in which ν_9 became infrared active as a result of site symmetry effects. The $\underline{t}_2\nu$(NiC) and δ(NiCO) modes are expected to interact considerably because of their proximity; however, a potential energy distribution calculation indicated that the lower of the two frequencies was definitely due to NiC stretching, while the higher frequency was primarily NiCO bending. The last remaining assignment to be made in the 700-300cm^{-1} region is that of ν_3, the doubly degenerate δ(NiCO) mode. It was first assigned tentatively at 461cm^{-1} by Jones,[9] *i.e.* coincident with $\nu_6(\underline{t}_2)$, and at 600cm^{-1} by Stammreich *et al.*[8] who preferred this assignment because by comparison with the Raman spectra of $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$,[7] $\nu_3(\underline{e})$ was expected to have a considerably higher frequency than $\nu_6(\underline{t}_2)$. Bigorgne and Bouquet[26] recently conducted a systematic study of $Ni(CO)_{4-n}L_n$ and $Ni(C^{18}O)_{4-n}L_n$, and *via* an extrapolation method, predicted that ν_3 lay at 380 ± 10cm^{-1}.

The currently accepted assignments for $Ni(CO)_4$ are summarized in Table II.

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* Throughout this thesis, fundamental modes and combinations (or overtones) will be designated by lower case and upper case letters, respectively.

TABLE II. LOW-FREQUENCY FUNDAMENTAL FREQUENCIES IN cm^{-1} OF $Ni(CO)_4$.[31]

Assignment			Gas	CCl_4soln.
$\underline{a}_1$	ν_2	ν(MC)	370.8	379.8
$\underline{e}$	ν_3	δ(MCO)	380	380
	ν_4	δ(CMC)	62	78
$\underline{t}_2$	ν_6	δ(MCO)	458.9	455
	ν_7	ν(MC)	423.1	422.5
	ν_8	δ(CMC)	79	91
$\underline{t}_1$	ν_9	δ(MCO)	...	300

ii. Penta-coordinated - $Fe(CO)_5$

Following $Ni(CO)_4$, $Fe(CO)_5$ is probably the most thoroughly studied metal carbonyl. Adams[1] states "the history of the $Fe(CO)_5$ is long and involved", while Edgell, Wilson, and Summitt[33] put it less mildly; "Considerable confusion exists regarding the infrared spectrum and the vibrational assignment in $Fe(CO)_5$". Two low-resolution infrared studies were first reported. The earlier one by Sheline and Pitzer[34] dealt with the 4000-460cm^{-1} region while the second one by O'Dwyer[35] in the 4000-400cm^{-1} region is misleading because of the presence of strong impurity bands which were assigned as fundamentals. The first far-infrared data (150-30cm^{-1}) on the liquid by Cotton *et al.*[36] were also shown to be partly erroneous.[37]

The presently accepted assignment for $Fe(CO)_5$ is shown in Table III. It was proposed by Edgell, Wilson, and Summitt,[33] and rests

TABLE III. VIBRATIONAL SPECTRUM OF IRON PENTACARBONYL.[1]

D_{3h}				Liquid	Vapour
ν_3	$\underline{a}_1'$	R	ν(FeC)	414	
ν_4			ν(FeC)	377	
ν_5	$\underline{a}_2'$	Inact.	δ(FeCO)	-	-
ν_7	$\underline{a}_2''$	i.r.	δ(FeCO)	615	620
ν_8			ν(FeC)	474	474
ν_9			δ(CFeC)	-	-
ν_{11}	$\underline{e}'$	i.r. + R	δ(FeCO)	638	646
ν_{12}			δ(FeCO)	552	544
ν_{13}			ν(FeC)	430	431
ν_{14}			δ(CFeC)	112	104
ν_{15}			δ(CFeC)	68	
ν_{16}	$\underline{e}''$	R	δ(FeCO)	752	
ν_{17}			δ(FeCO)	492	
ν_{18}			δ(CFeC)	104	95

mainly on their infrared data, and on the Raman data of Stammreich, Sala, and Tavares.[6] To assign the bands in the ν(FeC) - δ(FeCO) region, Edgell and his co-workers first divided them according to symmetry species by taking into account that, certain infrared frequencies had no Raman counterparts ($\underline{a}_2''$) and *vice versa* ($\underline{a}'$ or $\underline{e}''$), that certain did ($\underline{e}'$), and the selectivity of overtone and combination spectroscopic activities ($\underline{e}'$ and $\underline{e}''$). For the assignment of the frequencies to specific modes, mathematical expressions were derived for the frequency, intensity, and depolarization magnitudes of modes of the same symmetry. The two $\underline{e}'$ and the two $\underline{e}''$ δ(MCO) modes were assigned arbitrarily and no assignment was made for the inactive $\underline{a}_2'$ mode. One of the three Raman lines observed in the δ(CMC) region was assigned to one of the two expected $\underline{e}'$ modes, while the other two were arbitrarily assigned to the other $\underline{e}'$ and the $\underline{e}''$ mode.

iii. Octahedral - $M(CO)_6$

Early assignments for the fundamental frequencies of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were based almost entirely on infrared data.[3,4,29,38,39] Partial Raman spectra were first reported by Danti and Cotton,[40] but from a comparison of the infrared spectra of $Mo(CO)_6$ in the vapour phase and in chloroform solution Jones concluded that many of the Raman lines observed arose "from a solvent effect of some sort".[4a] Amster, Herman, and Tobin[41] made a complete Raman study of all three hexacarbonyls, both in the solid state and as saturated methylene chloride solutions, and also studied the infrared spectra of the crystalline complexes to 300cm^{-1}. It may be of interest to point out that the latter study indicated no bands which were not easily attributable to solute molecules, and no solid state splitting or extra bands arising from the lifting of the mutual exclusion principle were observed.[41] Jones[42] made use of the Raman data to correct some of his earlier assignments, and he, together with McDowell and Goldblatt[43] have recently published the results of a very thorough investigation on the vibrational spectra of the hexacarbonyls: $M(^{1}C^{k}O)_6$ (1,k = 12,16; 13,16; or 12,18, and M = Cr, Mo, or W).

Molecules of O_h symmetry, $M(CO)_6$, are expected to have thirteen fundamental vibrations, $2\underline{a}_{1g}(R) + 2\underline{e}_g(R) + \underline{t}_{1g}(IA) + 4\underline{t}_{1u}(i.r.) + 2\underline{t}_{2g}(R) + 2\underline{t}_{2u}(IA)$ which may be subdivided as follows:

$$\begin{aligned}
\Gamma_{CO} &= \underline{a}_{1g}(\nu_1) + \underline{e}_g(\nu_3) + \underline{t}_{1u}(\nu_6) \\
\Gamma_{MC} &= \underline{a}_{1g}(\nu_2) + \underline{e}_g(\nu_4) + \underline{t}_{1u}(\nu_8) \\
\Gamma_{MCO} &= \underline{t}_{1g}(\nu_5) + \underline{t}_{1u}(\nu_7) + \underline{t}_{2g}(\nu_{10}) + \underline{t}_{2u}(\nu_{12}) \\
\Gamma_{CMC} &= \underline{t}_{1u}(\nu_9) + \underline{t}_{2g}(\nu_{11}) + \underline{t}_{2u}(\nu_{13})
\end{aligned}$$

The rule of mutual exclusion[44] which applies to molecules with a center of symmetry facilitated the assignment of the observed infrared and Raman frequencies to specific modes. Observation of polarized Raman bands further helped the assignment of the latter. The overtone and combination modes were used to assign the remaining fundamental frequencies.

The latest assignments are shown in Table IV.

TABLE IV. LOW-FREQUENCY FUNDAMENTAL FREQUENCIES OF $M(CO)_6$ (M = Cr, Mo, W), in cm^{-1}.[43]

Assignment			$Cr(CO)_6$			$Mo(CO)_6$			$W(CO)_6$		
			Solid	CCl_4	Vapour	Solid	CCl_4	Vapour	Solid	CS_2	Vapour
$\underline{a}_{1g}$	ν_2	$\nu(MC)$	388.0	381.2	379.2	406.8	402.2	391.2	433.8	427.1	426
$\underline{e}_g$	ν_4	$\nu(MC)$	397.7	394	390.6	392.2	386	381	418.3	412	410
$\underline{t}_{1g}$	ν_5	$\delta(MCO)$	367.7		364.1	346.0		341.6	365.3		361.6
$\underline{t}_{1u}$	ν_7	$\delta(MCO)$		664.6	668.1		592.8	595.6		583.1	586.6
	ν_8	$\nu(MC)$		443.8	440.5		367.0	367.2		374.4	374.4
	ν_9	$\delta(CMC)$	104.0	103	97.2	91.8	91	81.6	90.7	92.0	82
$\underline{t}_{2g}$	ν_{10}	$\delta(MCO)$	533.1		532.1	476.5		477.4	485.0		482.0
	ν_{11}	$\delta(CMC)$	114.2	100.8	89.7	103.7	91	79.2	107.6	92.0	81.4
$\underline{t}_{2u}$	ν_{12}	$\delta(MCO)$			510.9	508.5		507.2	524		521.3
	ν_{13}	$\delta(CMC)$			67.9			66			61.4

iv. Polynuclear Metal Carbonyls

a. $Co_2(CO)_8$ and $Fe_2(CO)_9$

No detailed low-frequency study has been carried out on $Co_2(CO)_8$ although the $\nu(CO)$ region has been thoroughly investigated in order to help identify the natures of the isomers which are known to exist in solution.[45-48] $Co_2(CO)_8$ is known to have the structure shown in Figure 2-a in the solid state which in solution is in equilibrium with a metal-metal bonded isomer whose structure is probably that shown in Figure 2-b. Bor,[47] however, rules out this structure in preference to that shown in Figure 2-c. On the basis of the number of observed and expected bands for the i.r. spectra in the 700-300cm^{-1} region, Noack[49] favoured the D_{3d} structure.

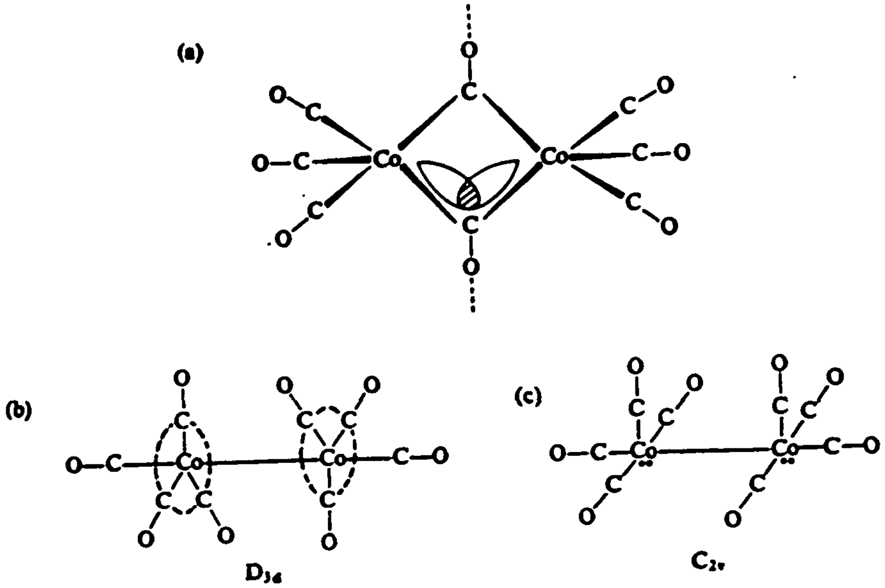

Figure 2.-Structure of $Co_2(CO)_8$; (a) in the solid-state and in solution, (b), (c) possible solution isomers.

Iron nonacarbonyl, $Fe_2(CO)_9$, is a yellow solid insoluble in all normal solvents.[1] It was first examined as a powder by Sheline and Pitzer,[50] and consequently the spectrum exhibited a strong Christiansen effect. The ν(CO) spectra were reported by Cotton, Liehr, and Wilkinson,[51] and by Fritz and Paulus[52] who also listed bands at 453,422 and 386cm^{-1} which they assigned to ν(FeC).

b. Dodecacarbonyls $Fe_3(CO)_{12}$,$Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$

An infrared study of $Fe_3(CO)_{12}$ in CS_2, CCl_4, and $CHCl_3$solutions yielded bands at 2080, 2034, 1828, 662, 597 and 557cm^{-1} and a D_{2d} structure of the form $(CO)_4Fe(CO)_2Fe(CO)_2Fe(CO)_4$ was proposed[53] in contradiction to a structure with bridging carbonyl groups as had been earlier deduced[54] The structure now accepted is shown in Figure 3-a.[55] The two bands around 600cm^{-1} were originally assigned to ν(FeC)[53] but are more likely to be δ(FeCO) modes.[1] More studies on this complex, both infrared and Raman would be highly desirable.

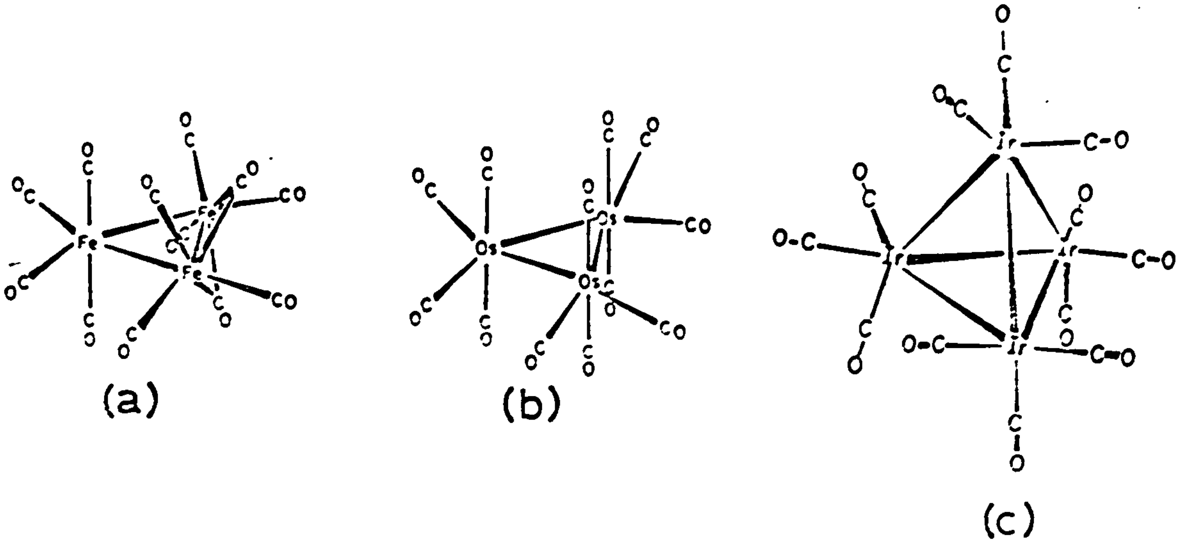

Figure 3.-Structures of dodecacarbonyls; (a) $Fe_3(CO)_{12}$, (b) $Os_3(CO)_{12}$ [and $Ru_3(CO)_{12}$], (c) $Ir_4(CO)_{12}$.

Both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are known to have the structure shown in Figure 3-b.[56] Two low-resolution studies were first performed on these complexes,[57,58] one of which assigned absorptions between 600-500cm^{-1} in the solid to ν(MC) modes[58] although no indication was given as to whether there were any higher frequency bands due to δ(MCO). Huggins, Flitcroft, and Kaesz[18] made a careful infrared investigation on $Os_3(CO)_{12}$ down to 290cm^{-1}. In the low-frequency region all ten predicted frequencies, four ν(OsC) and six δ(OsCO), were observed for the solid. The ν(OsC) were assigned *via* a comparison with the ν(CO) modes by taking account of the inverse bond order expected for M-C and C-O bonds, and by predicting that the spacing of the radial modes due to *cis* coupling would be less than that for the axial modes due to *trans* coupling. However, they concluded that a normal coordinate analysis would be necessary to clearly distinguish between the ν(OsC) and δ(OsCO). A later Raman, and infrared study to 300cm^{-1}, by Quicksall and Spiro[59] did not attempt to assign the modes in the 650-350cm^{-1} region, apart from dividing them into ν(MC) modes from 500 to 350cm^{-1}, and δ(MCO) modes from 650 to 500cm^{-1}. In this study, however, assignments were made for metal-metal stretching vibrations by noting changes in the Raman spectra below 200cm^{-1}. These were nearly identical except for two sharp, intense bands which shifted from 158 and 117cm^{-1} to 185 and 149cm^{-1} for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$, respectively. These assignments are in good agreement with those of Hartley, Kilty and Ware[60] who found bands at 161($\underline{a}'$) and 120($\underline{e}'$) for the osmium complex and at 185($\underline{a}'$) and 152($\underline{e}'$) for the ruthenium complex. Approximate force constant calculations for the modes below 200cm^{-1} indicated a definite frequency order which was used to assign the modes in this region specifically.[59]

Quicksall and Spiro,[61,62] also studied the Raman spectrum of $Ir_4(CO)_{12}$ (structure given in Figure 3-c) and assigned the three intense Raman modes at 208, 164, and 105cm^{-1} to the $\underline{a}_1$, $\underline{t}_2$, and $\underline{e}$ cluster modes, respectively.[61] All the frequencies predicted below 210cm^{-1} (three metal cluster and six metal-carbon deformation modes) were observed and assigned by means of an approximate force constant calculation similar to those performed for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. However, this required that the metal cluster mode at 106cm^{-1} be reassigned to a weak band at 131cm^{-1}.[62] Abel *et al.*[64] studied the solid-state infrared and Raman data for $Ir_4(CO)_{12}$ and assigned the five strong infrared absorptions in the 700-350cm^{-1} region to $\underline{t}_2$ fundamentals without attempting to separate them into specific ν(IrC) and δ(IrCO) modes. The only other definite assignment that was made was for the most intense Raman band in this region which was assigned to the $\underline{a}_1$ ν(IrC) vibration.

c. Decacarbonyls $M_2(CO)_{10}$ (M = Mn, Tc, Re) and $MnRe(CO)_{10}$

Partial or complete infrared and Raman data for the decacarbonyls in the low-frequency region have been provided by a number of authors.[2,19,20,65-72] Flitcroft, Huggins, and Kaesz[69] studied the infrared spectra of all the decacarbonyls including the mixed metal species $MnRe(CO)_{10}$ down to 290cm^{-1}, but assigned only the ν(MC) and δ(MCO) modes of $\underline{e}_1$ symmetry. The ν(MC) modes for $Mn_2(CO)_{10}$ have also been assigned by Parker and Stiddard[19] who assumed that the energy sequence of these modes would be the reverse of that for the CO stretching modes. Complete Raman data for $Re_2(CO)_{10}$ have been reported by Lewis *et al.*[66] and by Hyams, Jones, and Lippincott.[70] The latter also reported complete infrared data and assigned the majority of the expected fundamentals to the observed frequencies. Quicksall and Spiro[68] assigned the fundamentals below $200cm^{-1}$ for $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$ by carrying out approximate normal coordinate calculations which indicated a specific frequency ordering of the modes. The low temperature solid-state i.r. spectra below $300cm^{-1}$ and the Raman spectra below $700cm^{-1}$ have also been reported by Clark and Crosse[72] although no assignments were made.

The metal-metal stretching frequencies of the decacarbonyls have aroused particular interest,[66-68,70-73] and attempts have been made to calculate and compare the associated force constants.[68,72]

The overall picture is as yet quite unclear and a complete assignment will have to await further studies and possibly a full normal coordinate treatment.

B. CARBONYLATE IONS

The spectra of three sets of carbonylate ions have been investigated. They are: (1) the tetrahedral group, $Co(CO)_4^-$,[7,74] and $Fe(CO)_4^{2-}$[7,74] (2) the octahedral group $V(CO)_6^-$,[20,72,75] and $M(CO)_6^+$ (M = Mn,[20,72] Re[72,75]) and (3) the halocarbonyls $M'(CO)_5X^-$ [2,72] (M′ = Cr, Mo, W). The spectra of these ions have been compared with those of their respective neutral counterparts, namely $Ni(CO)_4$, $M'(CO)_6$ (M′ = Cr, Mo, W) and $M(CO)_5X$ (M = Mn, Re).

The Raman spectrum of aqueous solutions of $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ were reported by Stammreich *et al.*[7] and complemented by the aqueous solution and solid-state infrared spectra of Edgell *et al.*[74] These studies also reported spectra for the $HFe(CO)_4^-$ ion. Edgell *et al.*[76] reported in a separate article the infrared spectra of $HCo(CO)_4$ and $DCo(CO)_4$. Stammreich *et al.*[7] assigned all the fundamentals in $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ with the aid of normal coordinate analyses[7,77] which led to the conclusion that the order $\nu_3[\underline{e}, \delta(MCO)] > \nu_6[\underline{t}_2, \delta(MCO)] > \nu_7[\underline{t}_2, \nu(MC)]$ prevailed.

A detailed analysis of both the solid-state and solution infrared and Raman spectra of $V(CO)_6^-$ and $Re(CO)_6^+$ has been recently carried out by Abel *et al.*[75] In this work the spectra of the ions were compared to the spectra of the neutral hexacarbonyls. The $\nu(MC)$ modes were all specifically assigned by taking into account the spectroscopic selection rules and the appearance of a polarized band in the Raman spectrum of each ion. Although a reciprocal relationship in the $\nu(CO)$ and $\nu(MC)$ frequencies of $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ had been noted previously,[20] Abel *et al.*[75] pointed out that the mean MC stretching frequencies for the four hexacarbonyls: $V(CO)_6^-$: 406cm^{-1}, $Cr(CO)_6$: 406cm^{-1}, $W(CO)_6$: 407cm^{-1}, and $Re(CO)_6^+$: 408cm^{-1} were virtually identical, while all the CO stretching frequencies were raised considerably (about 70-130cm^{-1}) with each unit positive charge increase on the central metal. These results led to the conclusion that the decrease in π back-bonding expected on an increase in the nuclear charge was counterbalanced by an increase in the carbon-metal sigma bond order. Of the thirteen possible fundamentals Abel *et al.* assigned twelve for $V(CO)_6^-$ and eleven for $Re(CO)_6^+$. The low temperature solid-state i.r. and Raman spectra of $V(CO)_6^-$, $Mn(CO)_6^+$, and $Re(CO)_6^+$ have also been reported by Clark and Crosse,[72] but no assignments were made.

Spectra for the anionic pentacarbonyl halides have been reported in the infrared[2,72] and Raman[72] but apart from the metal-halogen and the doubly degenerate ν(MC) modes, no other assignments were offered. However, it was noted that the e ν(MC) vibrations for the anionic species, $M'(CO)_5X$, (M' = Cr, Mo, W; X = Cl, Br, I) lay 7-34cm^{-1} above those of the corresponding isoelectronic neutral species, $M(CO)_5X$, (M = Mn, Re), the corresponding ν(CO) vibrations being about 80-150cm^{-1} lower. The ν(MX) vibrations for the anions occurred at about 40cm^{-1} lower than those for the neutral species; and this, along with the fact that the metal-halogen stretching frequencies for $Mn(CO)_4X_2^-$ were in the same position as those for $Mn(CO)_5X$, led Bennett and Clark[2] to the conclusion that ν(MX), like ν(CO), are strongly dependent on the oxidation state of the metal atom but independent of the overall charge. Approximate force constant calculations for the metal-halogen bonds have also indicated that, as expected, the force constants are strongly dependent on the oxidation state of the metal.[72]

C. SUBSTITUTED METAL CARBONYLS.

i. Metal Carbonyls Substituted with Organic or Organometallic Ligands.

Bigorgne and his co-workers[10,13,14,78] have studied the solution or liquid Raman spectra of a variety of substituted nickel carbonyls $Ni(CO)_{4-n}L_n$ (n = 1-4, and L = organic phosphines, phosphites, arsines, etc.) in all of which the symmetric vibrations were readily identified by their polarization properties. It was observed that on going along the series for which n = 0,1,2,3, the $\nu(NiC)$ frequencies increased regularly and inversely to the $\nu(CO)$ frequencies. Force constants for the C-O and Ni-C bonds were also calculated and related to the bond orders in the various complexes. It was found that on substitution of CO in $Ni(CO)_4$ by L, the order of the ligands as a function of variations in the C-O and Ni-C force constants followed closely the order of basicity of L, *i.e.* the more basic L, the more the Ni-C bond is strengthened and the more the C-O bond is weakened. This explained the difficulty in attaining high degrees of substitution, especially with basic ligands, as well as the relative stabilities of $Ni(CO)_4$ and some of its derivatives. As an example of the latter, the bond orders for the Ni-C bonds in $Ni(CO)_4$, and $Ni(CO)(PCl_3)_3$, and $Ni(CO)(PMe_3)_3$ were found[10] to be 1.25, 1.40, and 1.85, respectively, thus accounting for the instability of the first two complexes in comparison with the third.

The i.r. spectra of substituted cobalt carbonyls of the type $[LCo(CO)_3]$[17] and $Hg[Co(CO)_3L]_2$[10] have been examined, as mentioned earlier (p. 3), as have the i.r. spectra of complexes of the type $(CO)_4CoM'X_3$ and $(CO)_5MnM'X_3$ [$M'X_3$ = $SiCl_3$, $Si(OMe)_3$, $SiPh_3$, $SiEt_3$, $GeEt_3$, $SnEt_3$, or $PbEt_3$].[79]

In the latter study the δ(MCO) modes were generally assigned by comparison with the bands for *trans*-L(CO)$_3$CoM'X$_3$. It was noted that ν(MC) remained almost constant when M' was varied (X being kept constant), but decreased when the electronegativity of X was increased (M' being kept constant), in agreement with the results[10] for the substituted nickel complexes discussed on the previous page.

The Raman spectra of M[Co(CO)$_4$]$_2$(M = Cd, Hg) salts in the low frequency region investigated by Stammreich *et al.*[80] helped identify the compounds as possessing D_{3d} symmetry, since they had a strong polarized line at 152cm^{-1} due to ν(CoMCo) which had no Raman active antisymmetric counterpart. Furthermore, the seven expected Raman shifts [three for ν(CoC) and four for δ(CoCO) modes] were all observed. The infrared spectra in *n*-hexane have also been recorded down to 350cm^{-1} by Noack[51] and compared to those of CoH(CO)$_4$ and Co$_2$(CO)$_8$ (isomer in solution) from which a clear similarity in structure is indicated.

Co(CO)$_3$NO was first investigated by Magee[81] whose study was extended and revised by a McDowell, Horrocks, and Yates.[82] The latter group used ^{15}N and ^{13}C-substitution to help in the assignments. For example, the bands at 594 and 565cm^{-1} which were found to shift to 591 and 555cm^{-1} in the spectra of ^{15}N labelled complexes were assigned to ν(CoN) and δ(CoNO), respectively. Analogy with the spectral assignments for Ni(CO)$_4$ and a study of the observed combinations and overtones helped assign the remaining modes. A normal coordinate analysis indicated that the CoN stretch, and the degenerate CoC stretch and CoNO bend had a large amount of mixed character, in contrast with the CO and NO vibrations which were relatively pure.

Adams,[15] as mentioned earlier (p. 3), examined the i.r. spectra of a large number of substituted metal carbonyls ranging from mono- to pentacarbonyl systems and assigned all the bands between 682-468cm^{-1} to δ(MCO) bending modes.

A study of $Mo(CO)_{6-n}L_n$ (n = 1,2) was performed by Poilblanc and Bigorgne[5] and some of the ν(MC) and δ(MCO) modes assigned. For complexes of the type $Cr(CO)_{6-n}L_n$ (n = 1,2,3), Magee *et al.*[83] noted bands around 650cm^{-1} which they assigned to ν(CrC), although it is now more or less certain that they are δ(CrCO) modes.[1]

The far-infrared spectra (550-100cm^{-1}) of eighteen metal carbonyl compounds containing tin-transition metal bonds have been investigated.[84] The Sn-metal stretching frequency was assigned for all the complexes, and in some cases assignments for ν(MC) and δ(MCO) modes were given.

The compounds $Mn_2(CO)_8L_2$ [L = PF_3, $P(OPh)_3$, $AsPh_3$, PPh_3, PEt_3] have been studied[19] in conjunction with $Mn_2(CO)_{10}$ and the ν(MC) modes assigned by assuming that they will be in an order opposite to that for the ν(CO) frequencies. When the $\underline{e}_1$ and $\underline{b}_2$ frequencies for complexes containing different ligands were plotted against the corresponding $\underline{e}_1$ and $\underline{b}_2$ ν(MC) frequencies, respectively, reasonable plots were obtained which are consistent with the fact that changes in the M-C bond multiplicity are reflected by changes in that of the C-O bond. Not all the expected δ(MCO) modes were observed and no correlation between these modes and the ν(CO) was found, the former being relatively insensitive to substitution as might be expected if the total Mn-C + C-O bond order remains approximately constant.

The infrared spectra in the 700-200cm^{-1} for a number of complexes of the type $Mn(CO)_{4-n}L_nX$(L = PPh_3, $AsPh_3$, py, dipy, p-tol; X = Cl, Br) have also been reported but no assignments were given.[2]

The ν(MC) and δ(MCO) modes were also identified but not specifically assigned in the complexes $Fe(CO)_3L_2HgX_2$, $Fe(CO)_3L_2$ and $Fe(CO)_4L$ (L = PPh_3, $AsPh_3$, $SbPh_3$),[85] whereas some of the δ(FeCO) and ν(FeC) modes were identified and assigned in the infrared spectra of $Fe(CO)_{3-n}L_nI_2$ (n = 0, 1,2) complexes.[86]

The assignment of the δ(MCO) modes by means of intensity arguments in $C_pFe(CO)_2L$ and *trans*-$CpMo(CO)_2(L)SnPh_3$[21] has been discussed already (p. 5).

ii. Halocarbonyls

The low frequency infrared and Raman spectra of halocarbonylmetal complexes will provide the subject matter for the balance of this part of the thesis. A comprehensive account of the work reported to date in this area will now be presented.

The first report on this subject was provided by Bennett and Clark[2] who studied the octahedral complexes $M(CO)_5X$[M = Mn(I), Re(I), Cr(O), Mo(O), or W(O); X = Cl, Br,or I] and $M(CO)_4X_2$[M = Fe(II) or Os(II); X = Cl, Br,or I]. It was known that the ν(CO) modes were very dependent on the oxidation state of the metal [ν(CO) decreases *ca.* 100cm^{-1} per unit decrease in oxidation state] and that for a given series ν(CO) generally increased with increasing electronegativity of the halogen. Therefore, these workers felt that it would be of interest to correlate the ν(MX), ν(MC) and ν(CO) vibrations for a closely related series of metal carbonyl halides and to investigate any dependence that the ν(MX) and ν(MC) modes might have on the oxidation state of the metal and the electronegativity of the halogen.

Three infrared active ν(MC) and four infrared active δ(MCO) vibrations are expected for the $M(CO)_5X$ species of C_{4v} symmetry, and in fact five to eight bands and shoulders were seen in the 650-340cm^{-1} region. However, only two specific assignments were made, one to the ν(MC) vibration of e̲ symmetry around 400cm^{-1}, on the basis of its intensity and similarity to bands in the infrared spectra of the $M(CO)_6$ complexes, the other to the strong δ(MCO) mode in the 600cm^{-1} region which was attributed to a δ(MCO) vibration similar to the i.r. active $\underline{t}_{1u}$ δ(MCO) mode in the Group VIB metal hexacarbonyls. As noted in the section on carbonylate ions (p. 19) the e̲ ν(MC) vibrations of the anionic halopentacarbonyls were found to lie 7-34cm^{-1} above those for the corresponding isoelectronic neutral complexes. However, not all of the bands in the 650-340cm^{-1} region followed this order.

The lowest frequency band in *cis*-$Fe(CO)_4X_2$ in the δ(MCO) - ν(MC) region was found to increase by 7cm^{-1} with each change in halogen from chlorine to iodine, and was thus assigned to a ν(MC) vibration. No other conclusions were reached on the vibrational assignments for these compounds. (The effect on the ν(MX) frequencies has been discussed previously. See section on carbonylate ions.)

The infrared spectra of the three halopentacarbonylmanganese complexes were later reported by Cattrall and Clark[20] for cyclohexane and carbon tetrachloride solutions, but no new assignments were made.

The next attempt at analyzing the spectra of the $Mn(CO)_5X$ complexes was reported by Valenti *et al.*[87] who studied the spectra below $300cm^{-1}$ and assigned the $\nu(MX)$ stretching modes and the $\delta(CMnC)$ and $\delta(CMnX)$ bending modes by means of a simplified normal coordinate calculation. The authors stressed the need for Raman data on these complexes before any reasonable assignment could be made and suggested that infrared spectra using polarized light on oriented crystals could also prove useful.

The first complete assignment for a $M(CO)_5X$ compound was made for $Re(CO)_5I$ by Hyams, Jones, and Lippincott[70] who reported complete infrared and Raman data for this compound in the solid-state as well as partial solution spectra. These workers also carried out a force constant calculation in order to provide a rough idea on the extent of coupling between the vibrations and the relative ordering of the various predicted modes.

The bands below $200cm^{-1}$ were assigned where possible by comparison of the spectra of $Re(CO)_5I$ with that of $Re_2(CO)_{10}$. In this region two $\underline{a}_1$ modes are expected, one for $\nu(ReI)$ and the other for $\delta(CReC)$. The polarized Raman band at $165cm^{-1}$ was assigned to the former since it was non-existent in $Re_2(CO)_{10}$; while the band near $130cm^{-1}$ was assigned to the latter since it was coincident with a band at $128cm^{-1}$ in $Re_2(CO)_{10}$. Although of the four other Raman bands ($\underline{b}_1 + \underline{b}_2 + 2\underline{e}$) expected and observed in this region, the two $\underline{e}$ modes should be coincident with bands in the infrared spectrum, this was not found to be the case. The explanation given for this was that if site group splitting occurred in the solid-state, then the $\underline{e}$ mode would be split into two components which could be the Raman band at $120cm^{-1}$ and the infrared band near $107cm^{-1}$. These frequencies were assigned to δ(CReC) modes since the δ(CReI) frequency was expected to be the lowest in the spectrum, (*viz.* $42cm^{-1}$). The other δ(CReC) $\underline{e}$ mode was assigned to the infrared band near $95cm^{-1}$. The Raman active $\underline{b}_1$ and $\underline{b}_2$ δ(CReC) vibrations were calculated to lie between 40 and $80cm^{-1}$, the former being about $20cm^{-1}$ lower than the latter. These modes were assigned to the bands at 58 and $78cm^{-1}$, respectively.

The assignment of the δ(ReCO) bending modes was assisted by a calculation which indicated the order $\underline{b}_2 > \underline{b}_1 > \underline{a}_2$ for these vibrations. They were therefore assigned to bands at 610, 590, and $550cm^{-1}$, respectively. The strong band in solution at $587cm^{-1}$ was split into two components in the solid-state spectrum and was easily assigned to one of the $\underline{e}$ vibrations. The other $\underline{e}$ vibrations remained indeterminate. The band at $495cm^{-1}$ which appeared in both the infrared and Raman spectra was assigned to the $\underline{a}_1$ δ(ReCO) mode.

The ν(ReC) modes were all assigned by comparison with the spectrum of $Re_2(CO)_{10}$. One discrepancy in the assignment was that the $\underline{b}_1$ ν(ReC) mode was assigned to a band at $477cm^{-1}$ in the Raman spectrum but was predicted at $365cm^{-1}$ by the calculations. Although this disagreement was explained as arising from the effect of the iodine atom on the Re-C bonds, no mention was made as to how this inherent cause of error would affect the other calculated values and, in fact, the whole frequency order obtained.

The potential energy distribution calculation yielded the following results for the $\underline{b}_1$ fundamentals; $2089cm^{-1}$: 96% CO stretching and 4% ReC stretching; $580cm^{-1}$: 78% ReCO bending, 12% CReC bending, and

10% CReI bending; 485cm^{-1}: 98% ReC stretching and 2% CO stretching; 57cm^{-1}: 54% CReC bending, 43% CReI bending, and 3% ReCO bending. It seems strange that no ν(ReC) and δ(ReCO) contributions were calculated for the bands at 580 and 485cm^{-1}, respectively, in view of their proximity.

The far-infrared spectra of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ were next investigated by Adams and Squire.[71] The three polarized Raman bands in methanol solution which they observed for $Mn(CO)_5Br$ at 220, 383, and 473cm^{-1} were assigned to the $\underline{a}_1$ modes for Mn-X, Mn-C (equatorial), and Mn-C (axial), respectively.* The infrared bands around 545, 630, and 650cm^{-1} were all assigned to δ(MnCO) modes of $\underline{e}$ symmetry. Below 150cm^{-1}, the four expected infrared bands [δ(CMnC): $\underline{a}_1$ + 2$\underline{e}$; δ(CMnX): $\underline{e}$] and three of the six expected Raman bands [δ(CMnC): $\underline{a}_1$ + $\underline{b}_1$ + $\underline{b}_2$ + 2$\underline{e}$; δ(CMnX): $\underline{e}$] were observed, although two more were readily placed from the i.r. spectrum. The i.r. band near 120cm^{-1} showed a notable intensity difference in the spectra of the chloride and bromide complexes and was therefore assigned to the δ(CMnX) $\underline{e}$ mode. Of the CMnC bending fundamentals, only the symmetric $\underline{a}_1$ modes were assigned uniquely to bands near 100cm^{-1}, while bands around 115cm^{-1} in the Raman spectra, with no counterparts in the i.r. spectra were assigned to either the $\underline{b}_1$ or $\underline{b}_2$ δ(CMnC) modes. The remaining bands were given tentative assignments.

Another vibrational assignment for the halopentacarbonylmanganese complexes has recently been proposed by Hyams and Lippincott[88] who examined the infrared and Raman spectra of all three complexes. These workers based their assignments on a comparison of the spectra of $Mn(CO)_5X$ with that of

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* "Equatorial" (or radial) refers to the four CO groups in a plane, while "axial" refers to the single CO group *trans* to the halogen.

$Re(CO)_5I$ which they had reported previously.[70] They indicated that symmetry required the $\underline{b}_1$, $\underline{b}_2$, and $\underline{a}_2$ modes to be insensitive to changes in the mass of the metal atom. All other things being equal, any differences could thus be attributed to differences in force constants. Here again is an example of the use of the comparative technique in providing viable assignments.

The strong infrared bands observed near $640cm^{-1}$ for $Mn(CO)_5X$ were compared to those near $580cm^{-1}$ in $Re(CO)_5I$. The solid-state splitting for the former at -196°, the corresponding Raman components, and the position of the bands all pointed to a δ(MnCO) $\underline{e}$ mode. Three bands were resolved between 630 and $660cm^{-1}$, the highest of which (between 650 and $655cm^{-1}$) was assigned to the $\underline{a}_1$ δ(MnCO) mode because (1) it did not appear at that position in $Re(CO)_5I$ (2) there was a corresponding weak Raman band, and (3) if it were an $\underline{e}$ mode, Fermi resonance with the other bands in this region would be expected to complicate the spectra more than was actually observed. The band around $540cm^{-1}$ was assigned to one of the δ(MnCO) $\underline{e}$ modes by taking note of the spectroscopic selection rules for this region. The very weak bands around $600cm^{-1}$ were assigned by analogy to a weak Raman band in $Re(CO)_5I$ to a $\underline{b}_2$ MnCO bending mode. Of the ν(MnC) modes, only the symmetric vibrations were definitely assigned, the other assignments being somewhat tentative.

For the bands observed below $190cm^{-1}$ the Raman and infrared data for $Mn(CO)_5Br$ and comparison with $Re(CO)_5I$ suggested that the band at $75cm^{-1}$ for the chloride, $50cm^{-1}$ for the bromide, and $35cm^{-1}$ for the iodide could be assigned to the δ(CMnX) modes. While pointing out that mixing with lattice modes and the broadness of the Raman bands near $120cm^{-1}$

complicated the assignment of the bands, a tentative assignment for the remaining δ(CMnC) modes was suggested.

The studies just discussed will be compared and contrasted with our own results for the spectra of the halopentacarbonylmanganese complexes in Chapter III.

Other reports on halocarbonylmetal complexes include very incomplete infrared spectra reported for *cis*-$Fe(CO)_4X_2$ (X = Cl,[2] Br,[2,89] I,[2,89,90]) and *cis*-$Os(CO)_4X_2$ (X = Cl, Br).[2] It was found[89] that the average ν(FeX) frequency for these complexes was 5-11cm^{-1} above ν(MnX) for $Mn(CO)_5X$ complexes and the oxidation state dependence in the sense Fe(II) > Mn(I) was noted to be significant since it occurred despite an opposing mass effect. The spectra of *trans*-$Fe(CO)_4I_2$ and complexes of the type $Fe(CO)_{4-n}L_nI_2$ (n = 1,2,3) have also been reported.[90]

The halogen bridged complexes of the type $[M(CO)_4X]_2$ (M = Mn, Tc, Re; X = Cl, Br, I) have been studied by Kaesz and his co-workers.[9,92] The Mn and Re complexes have also been examined by Sartorelli, Valenti, and Zingales.[93] Flitcroft and Kaesz[91] found on comparison of the spectra, that changing X from Cl to I caused a shift to higher energies of the absorptions between 450 and 400cm^{-1} which was exactly in the opposite direction to the CO shifts, while the bands in the region around 550cm^{-1} and above were observed to shift very little or not at all with these substitutions. However, changing the metal from Mn through Tc to Re keeping X constant produced a shift in both sets of bands but the shift in the lower region (450-400cm^{-1}) was about twice that in the higher region (near 550cm^{-1}) indicating that the MC stretches were concentrated more in the lower lying regions. Sartorelli, Valenti, and Zingales[93] made assignments in the region 700-50cm^{-1} for the MC, and MX stretching and MCO bending vibrations. Approximate force constants calculated for the M-X bond in these compounds were found to be lower than those calculated for the $M(CO)_5X$ molecules.

Finally, mention may be made of the infrared spectra below 200cm^{-1} which have been measured and assigned for the complexes $Os_3(CO)_{12}X_2$(X = Cl, Br, I) and possible structures discussed.[60]

CHAPTER III. LOW-FREQUENCY STUDIES ON THE HALOPENTACARBONYLMANGANESE(I) DERIVATIVES

A. INTRODUCTION

From the account given in Chapter III, it is apparent that the low-frequency regions in the infrared and Raman spectra of metal carbonyls have received an increasing amount of attention in recent years. In an effort to extend the studies already reported on the low-frequency spectra of the halopentacarbonylmanganese(I) derivatives,[2,20,87,94] the solid-state and carbon disulfide solution infrared as well as the solid-state Raman spectra of these complexes were investigated in the region 700-33cm^{-1}. While the results of this investigation were being prepared for publication, and shortly after its actual publication,[95] a number of other workers reported their assignments for the low-frequency vibrational spectra.[71,72,88] Their results will be compared and contrasted with those for this study. In addition, the overtone and combination spectra in the regions 2800-2250 and 1350-700cm^{-1} were measured and their use in assigning some of the low-frequency fundamentals will be discussed.

Although the solid-state laser Raman spectra of the $Mn(CO)_5X$ derivatives in the CO stretching region had been reported[72,96] high resolution studies in the present work indicated that certain of the lines reported for $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ could be split into well defined doublets, (this has now been confirmed by another group of workers[88]). Since the $Mn(CO)_5X$ derivatives are known to be readily decomposed thermally to form the dimeric $[Mn(CO)_4X]_2$ derivatives,[97] the additional lines observed in the Raman spectra of the chloride and bromide were feared to have been due to the presence of some of the dimers as impurities which had been formed by thermal decomposition induced by the laser beam. In order to test this possibility the solid-state Raman spectrum of $[Mn(CO)_4Br]_2$ was recorded and compared with that of $Mn(CO)_5Br$. From this comparison, the chance of any decomposition occurring while the spectrum of $Mn(CO)_5Br$ was being recorded was quickly ruled out. Since definite splittings were also observed in the CO stretching region of the solid-state i.r. spectra of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$,it appears most likely that the splittings in both the Raman and the i.r. spectra were the result of correlation effects. With this in mind, the solid-state spectra of the $Mn(CO)_5X$ derivatives will be discussed in terms of the recently determined crystal structure of $Mn(CO)_5Cl$.[98]

The solid-state i.r. spectrum of $[Mn(CO)_4Br]_2$ and the solid-state i.r. and Raman spectra of $[Mn(CO)_4I]_2$ were also recorded and the results are found to be in accord with the D_{2h} symmetry expected.

B. RESULTS AND DISCUSSION

The crystal and molecular structure of $Mn(CO)_5Cl$ has recently been determined.[98] The space group is *Pnma*(D_{2h}^{16}) and there are four molecules per unit cell. The site symmetry of the molecules is C_s. The molecular symmetry is C_s, but the deviations from C_{4v} are within experimental error. $Mn(CO)_5Br$ is isomorphous[99] with $Mn(CO)_5Cl$ and so, presumably, is $Mn(CO)_5I$.

The vibrational representation for an isolated $Mn(CO)_5X$ molecule of C_{4v} symmetry reduces as follows:

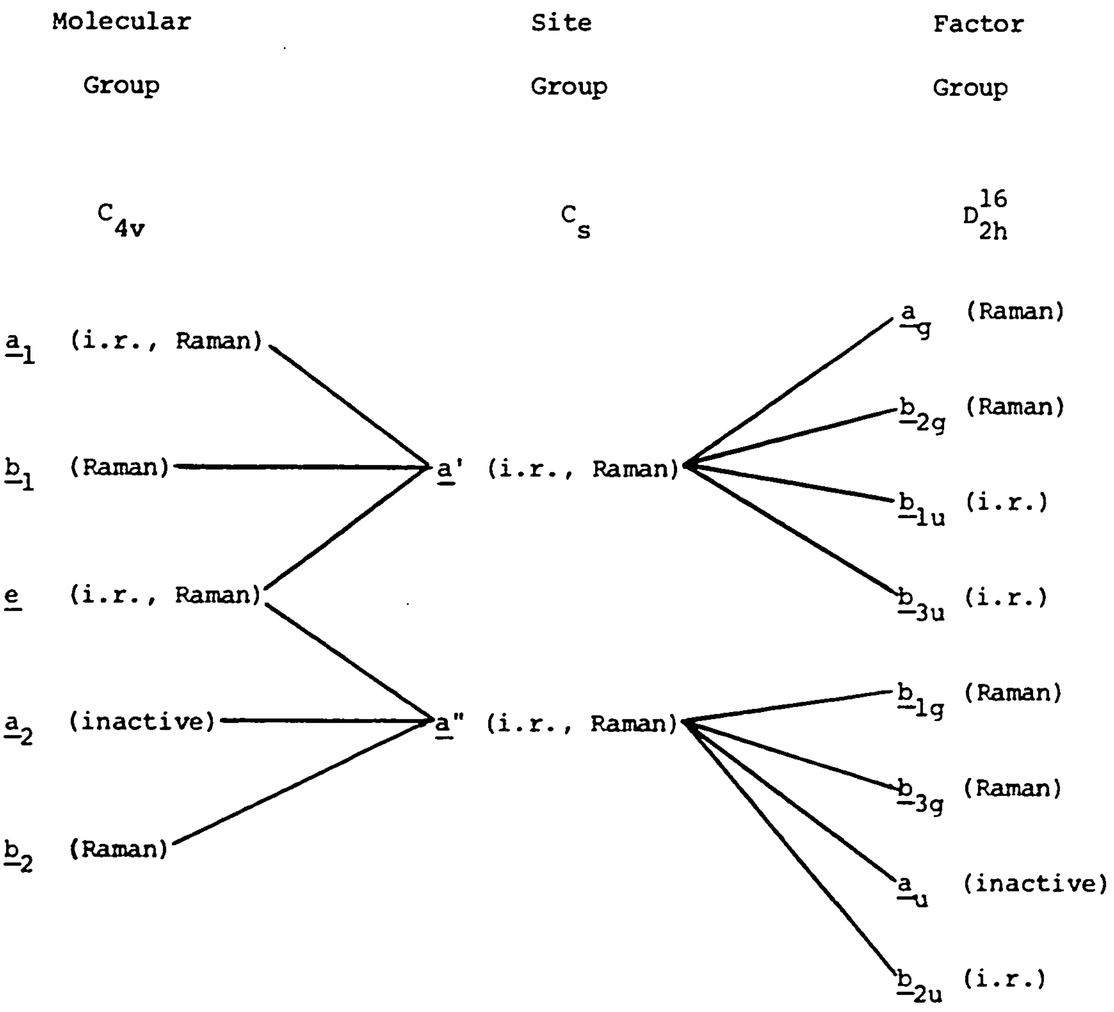
$$\Gamma_{vib}^{C4v} = 7\underline{a}_1 + 4\underline{b}_1 + 8\underline{e} + \underline{a}_2 + 2\underline{b}_2$$

The correlation between the C_{4v} symmetry of the free molecule, the C_s site symmetry, and the D_{2h}^{16} symmetry of the crystal is shown in Table V together with the spectroscopic activity. The factor group D_{2h}^{16} is isomorphous with the corresponding point group D_{2h}. From the correlation diagram it can be seen that non-degenerate modes in the free $Mn(CO)_5X$ molecule could be split into four components (two i.r. and two Raman active) in the crystal and the doubly degenerate modes into eight (four i.r. and four Raman active). Furthermore, the irreducible representations for the internal and external optically active vibrational modes of crystalline $Mn(CO)_5X$ are given by

$$\Gamma_{vib}^{D2h} = 19\underline{a}_g + 19\underline{b}_{2g} + 19\underline{b}_{1u} + 19\underline{b}_{3u} + 11\underline{b}_{1g} + 11\underline{b}_{3g} + 11\underline{b}_{2u}$$

for the internal modes and

TABLE V. CORRELATION BETWEEN THE VARIOUS SYMMETRIES ASSOCIATED WITH THE $Mn(CO)_5X$ MOLECULES.[a]



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[a] For the correlation between C_{4v} and C_s, σ_v was used; for that between D_{2h} and C_s, $\sigma(zx)$ was used.

$$\Gamma^{D2h}_{vib} = 3\underline{a}_g + 3\underline{b}_{2g} + 2\underline{b}_{1u} + 2\underline{b}_{3u} + 3\underline{b}_{1g} + 3\underline{b}_{3g} + 2\underline{b}_{2u}$$

for the external modes.

In the treatment of the vibrational spectra of the $Mn(CO)_5X$ molecules, therefore, it is important to know whether or not any correlation splitting occurs in the solid-state spectra, and also whether or not any of the frequencies observed below $150cm^{-1}$ result from external rather than internal modes.

The only compound whose i.r. spectrum was measured in CS_2 solution and in the solid-state was $Mn(CO)_5I$. The observed frequencies are given in Table VI. There was no difference between the spectrum of the solution and that of the solid, apart from some small frequency shifts. (The slight differences in the overtone and combination regions are excluded from the discussion). The observed frequencies for the solid-state i.r. spectra of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ are also given in Table VI. These are rather complex in the CO stretching region by comparison to the reported solution spectra.[99] Other research groups who have investigated the solution and solid-state i.r. spectra of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ throughout the various spectral regions found that differences only occurred in the CO stretching region.[2,20,72,88,94]

Solution Raman spectra of the $Mn(CO)_5X$ compounds were not measured in this study. Other workers have experienced considerable difficulty in measuring solution spectra of the compounds in the low-frequency region,[71,72,88] with only a fraction of the expected number of bands being observed, but fortunately solution spectra in the CO stretching region have proved more readily obtainable.[88,99] Solid-state Raman data for the CO stretching region have been published recently,[72,88,96]

TABLE VI. VIBRATIONAL SPECTRA OF $Mn(CO)_5X$(X = Cl, Br, I)(cm^{-1})[a]

X = Cl		X = Br		X = I			
i.r. (solid)[c]	Raman (solid)	i.r. (solid)	i.r. (solid)	i.r. (solid)	i.r. (CS_2)	Raman (solid)	Assignment[b]
		50vw	54m			45msh	*e* δ(CMnX), ν_{22}
		64vw					*b*$_1$ δ(CMnC), ν_{12} ?
(79w)		88w		98w			*e* δ(CMnC), ν_{20} or ν_{21}
(102m)		103m	100s	107m			*a*$_1$ δ(CMnC), ν_7
(115w)	112s						*b*$_2$ δ(CMnC), ν_{14} ?
(127s)	125s	123s	117s	116m		122vs	*e* δ(CMnC), ν_{20} or ν_{21}
(143m)	132s	133ms		137m		133vs	*e* δ(CMnC), ν_{20} or ν_{21}
(295s)	291s	222s	219s	188s		190vs	*a*$_1$ ν(MnX), ν_6
	382vs		385s	386vw		389vs	*a*$_1$ ν(MnC), (radial), ν_5
409s	408w	408m		406ms	410m[g]	413w	*a*$_1$ ν(MnC), (axial), ν_4
418s		415s 422s	415	427s	431vs	425mw	*e* ν(MnC), ν_{19}
478w	477s	471w	475m	467w	464w	466m	*a*$_1$ δ(MnCO), ν_3
∿535[d]	534vw	∿535[d]		∿525[d]	∿525[d]		*a*$_2$ δ(MnCO), ν_8

TABLE VI (Cont'd)

550s	548vw	547m	540ms	544m	547w	544w	e	δ(MnCO), ν_{18}
					608w		?	
	628w		630w	~620^d			b_2	δ(MnCO), ν_{13} ?
638vs	640vw	638vvs	638w	638vs	641s	633ms	e	δ(MnCO), ν_{17}
654ssh	649vw	651ssh	650w	652ssh	651m		e	δ(MnCO), ν_{16}
					695vw			ν_{17} + (54?)
					713vw			ν_{17} + (72?)
					730vw			ν_{17} + (89?)
				794vw	794vw			137 + ν_{16}
785s		795s		812m	813m			$\nu_5 + \nu_{19}$; $\nu_4 + \nu_5$
810msh		813msh						$2\nu_4$
		881msh		871w	876w			$\nu_3 + \nu_4$
900s		900s		900s	897s			$\nu_3 + \nu_{19}$
914m				920w				$\nu_5 + \nu_8$?
954m		951m		945ms	951w			$\nu_4 + \nu_{18}$; $\nu_8 + \nu_{19}$
				966w	973w			$\nu_{18} + \nu_{19}$
988m		986m		990m	1000s			$\nu_{10}{}^e + \nu_{19}$; $\nu_{11}{}^f + \nu_{17}$
1003wsh		1002vw		1001vw				$\nu_5 + \nu_{13}$; $\nu_{11}{}^f + \nu_{16}$
		1018wsh?		1019vw				$\nu_3 + \nu_{18}$

TABLE VI (Cont'd)

1049m		1040m		1035s	1047s		$\nu_4 + \nu_{17}$
1063m		1053m		1050m			$\nu_4 + \nu_{16}$
1079m		1077m		1079m	1087m		$\nu_{16} + \nu_{19}$
		1128vw		1125vw	1127w		$\nu_3 + \nu_{16}$
1175m		1170m		1169m			$\nu_8 + \nu_{17}$; $\nu_{13} + \nu_{18}$
		1187m		1184sh	1181m		$\nu_{17} + \nu_{18}$
1264w							$2\nu_{13}$; $\nu_{13} + \nu_{17}$
1281w		1275w			1280w		$2\nu_{17}$
1302w							$2\nu_{16}$
1988m 2001m	1983ms,sh 1985s	1992s 2002m	1989ms 1993s	2002m	2005m	2005s	$\underline{a}_1$ (CO) (axial), ν_2^i
2050s	2076s	2049s	2078s	2043s	2045s		$\underline{e}$ (CO), ν_{15}
						2070s	
2073m 2086m	2091s	2068m 2081m	2090ms 2093ms		2080^h		$\underline{b}_1$ (CO), ν_9^j
2144w	2141s	2139w	2142s	2132w	2127w	2133s	$\underline{a}_1$ (CO) (radial), ν_1

2435s	2434s	2438s	2444s	$\nu_5 + \nu_{15}$
2474s	2468s	2472s	2476s	$\nu_2 + \nu_3$; $\nu_{15} + \nu_{19}$
2503s	2501s	2507s	2504s	$\nu_9 + \nu_{19}$
	2548w	2536w	2535w	$\nu_2 + \nu_{18}$
2554m	2556m	2558m	2558m	$\nu_1 + \nu_{19}$
	2580w			$\nu_8 + \nu_{15}$; $\nu_2 + \nu_{10}^e$
			2590w	$\nu_{15} + \nu_{18}$
			2644w	$\nu_2 + \nu_{17}$
2726w	2720w	2716w	2710w	$\nu_9 + \nu_{17}$
2780w	2772w	2762m	2767m	$\nu_1 + \nu_{17}$
2798w	2789w	2776w		$\nu_1 + \nu_{16}$

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[a] Each list of frequencies has been divided into several sections and the intensities given are relative to the most intense peak within each section.

[b] The frequency designations are from ref. 77.

[c] The spectrum was not measured below 300cm^{-1} - the frequencies shown in parentheses are from ref. 72.

[d] Predicted from combination spectra.

[e] $\underline{b}_1$ δ(MnCO) predicted at ∿570(Cl), ∿570(Br), and ∿565(I).

[f] $\underline{b}_1$ ν(MnC) predicted at ∿350 (Cl, Br and I).

[g] In *n*-hexane solution.

[h] From ref. 99.

[i] The split $\underline{a}_1$ modes are assigned as: ($\underline{b}_{1u}$ + $\underline{b}_{3u}$) - i.r. active; ($\underline{a}_g$ + $\underline{b}_{2g}$) - Raman active.

[j] The split $\underline{b}_1$ modes are assigned as: ($\underline{b}_{1u}$ + $\underline{b}_{3u}$) - i.r. active; ($\underline{a}_g$ + $\underline{b}_{2g}$) - Raman active.

and the solid-state spectra in this region were also studied in the work described here. A comparison of the results with those already published is given in Table VII. The spectrum of $Mn(CO)_5Br$ recorded under both low and high resolution in this study is shown in Figure 4. For C_{4v} symmetry, four Raman active CO modes ($2\underline{a}_1 + \underline{b}_1 + \underline{e}$) are expected, and from i.r. studies involving force constant calculations,[100,101] these modes decrease in frequency in the order*

$$\underline{a}_1 \text{ (radial)} > \underline{b}_1 > \underline{e} > \underline{a}_1 \text{ (axial)}$$

Reference to Table VII shows that Cotton, Musco, and Yagupsky[99] observed four strong Raman lines for $Mn(CO)_5Br$ in CS_2 and in n-hexane solution, while Hyams and Lippincott[88] observed seven such lines in solution, only four of which they assigned to fundamentals. Clark and Crosse[94] found four strong lines and one very weak line in the solid-state spectrum of the same compound. In this work the solid-state spectrum of $Mn(CO)_5Br$ was recorded under high resolution and six strong lines and no weak lines were observed. It is apparent that, in addition to some fairly large frequency shifts there are two new lines in going from the solution spectrum of $Mn(CO)_5Br$ to that of the solid. These new lines resulted from small splittings in the $\underline{a}_1$ (axial) and $\underline{b}_1$ modes. Hyams and Lippincott[88] have recently confirmed these splittings under high resolution. The splittings may have been the result of correlation effects; the correlation diagram in Table V, indicating that modes of $\underline{a}_1$ or $\underline{b}_1$ symmetry in the free molecule could be split into two Raman components ($\underline{a}_g + \underline{b}_{2g}$) in the crystal. The $\underline{a}_1$ (axial) mode of $Mn(CO)_5Cl$ was also observed to be split in the solid-state spectrum, but no splittings at all could be detected in the spectrum of $Mn(CO)_5I$ which is shown in Figure 5. The latter was

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* The terms "radial" and "axial" have been defined in the footnote on p. 28.

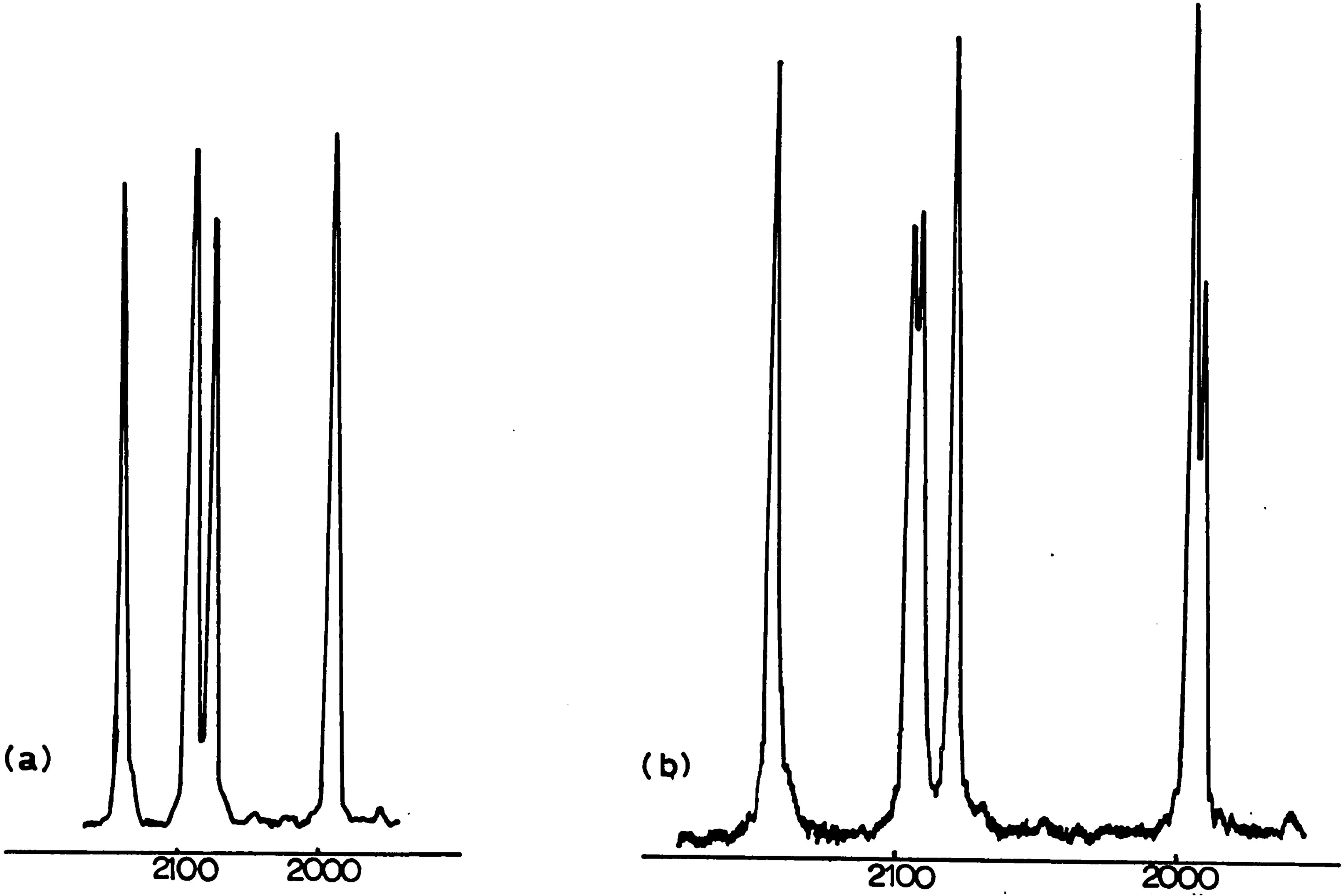

Figure 4.-Raman spectrum of $Mn(CO)_5Br$ (solid) in the CO stretching region; (a) Slit width $5cm^{-1}$, (b) Slit width $1cm^{-1}$

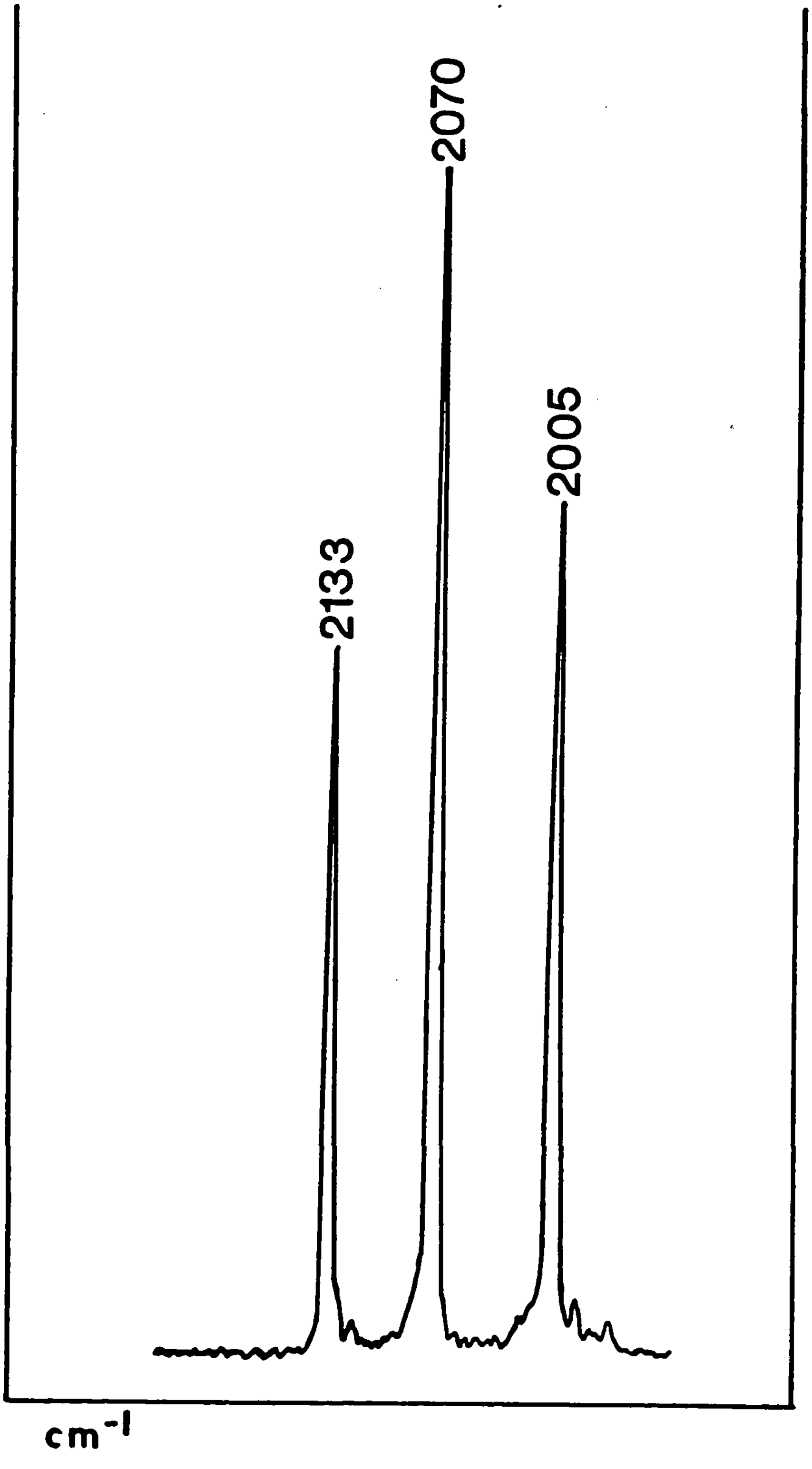

Figure 5.-Raman spectrum of $Mn(CO)_5I$ (solid) in the CO stretching region.

TABLE VII. RAMAN SPECTRA OF THE $Mn(CO)_5X$ DERIVATIVES IN THE CO STRETCHING REGION (cm^{-1})

		Davison and Faller[96,a,b]	Cotton, Musco, and Yagupsky[99,a,c]	Clark and Crosse[72,b]	Hyams and Lippincott[88,b]	This work[b]
$Mn(CO)_5Cl$	a_1 (radial)			2143ms	2149s	2141s
	b_1			2092s 2077ms	2098svs 2082svs	2091s
	e			2046w	2052w	2076s
	a_1 (axial)			1986s	1993vs 1988sh	1985s 1983ms,sh
$Mn(CO)_5Br$	a_1 (radial)	2137s	2133	2138s	2139vs 2133sh	2142s
	b_1	2086s	2080	2088s 2074ms	2089s 2087s 2074vs	2093ms 2090ms
	e	2072s	2051	2045vw	2043vw	2078s
	a_1 (axial)	1984s	2000	1989s	1989vs 1986m	1993s 1989ms
$Mn(CO)_5I$	a_1 (radial)			2130ms	2134s	2133s
	b_1[d]			2072s	2075vs	
	e					2070s
	a_1 (axial)			2004ms	2007vs	2005s

[a] No assignments proposed in this work.

[b] Solid-state spectra.

[c] CS_2 and *n*-hexane solution spectra, no relative intensities given.

[d] Observed at 2072cm^{-1} in cyclohexane solution.[101]

unique in that only three lines were observed. The two outermost lines were readily assigned as the two $\underline{a}_1$ modes since they were coincident with infrared bands previously designated as $\underline{a}_1$ vibrations. The third line was in the region where the $\underline{b}_1$ mode was expected, it therefore appears that in this case either the $\underline{b}_1$ and $\underline{e}$ modes are accidentally degenerate or that the $\underline{e}$ mode was too weak to be observed. Three lines were also only observed in the CO stretching region in the other studies performed on the iodide.[72,88]

It was felt that before the splittings in the solid-state Raman spectra of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ could be attributed to correlation effects, there was one other possibility which had to be considered. The $Mn(CO)_5X$ compounds are readily thermally decomposed to the dimeric $[Mn(CO)_4X]_2$ compounds[97] and it was thought possible that the laser beam could cause such decompositions to take place, resulting in the appearance of additional lines in the Raman spectra. In view of this, the solid-state laser Raman spectra of $[Mn(CO)_4Br]_2$ was recorded in both the CO stretching and the low-frequency regions. The solid-state Paman spectrum of $[Mn(CO)_4I]_2$ was studied in the same regions for comparative purposes. The spectrum of the dimeric chloro-compound was not investigated. Both $[Mn(CO)_4Br]_2$ and $[Mn(CO)_4I]_2$ proved to be extremely poor scatterers and only a few lines could be clearly discerned above the noise level. The observed frequencies are given in Table VIII, while the spectrum in the CO region of $[Mn(CO)_4Br]_2$ is shown in Figure 6. A comparison of the CO stretching frequencies of $Mn(CO)_5Br$ and $[Mn(CO)_4Br]_2$ immediately reveals that no detectable amount of the dimer was being formed while the spectrum of the pentacarbonyl was being recorded. Even without the obvious differences

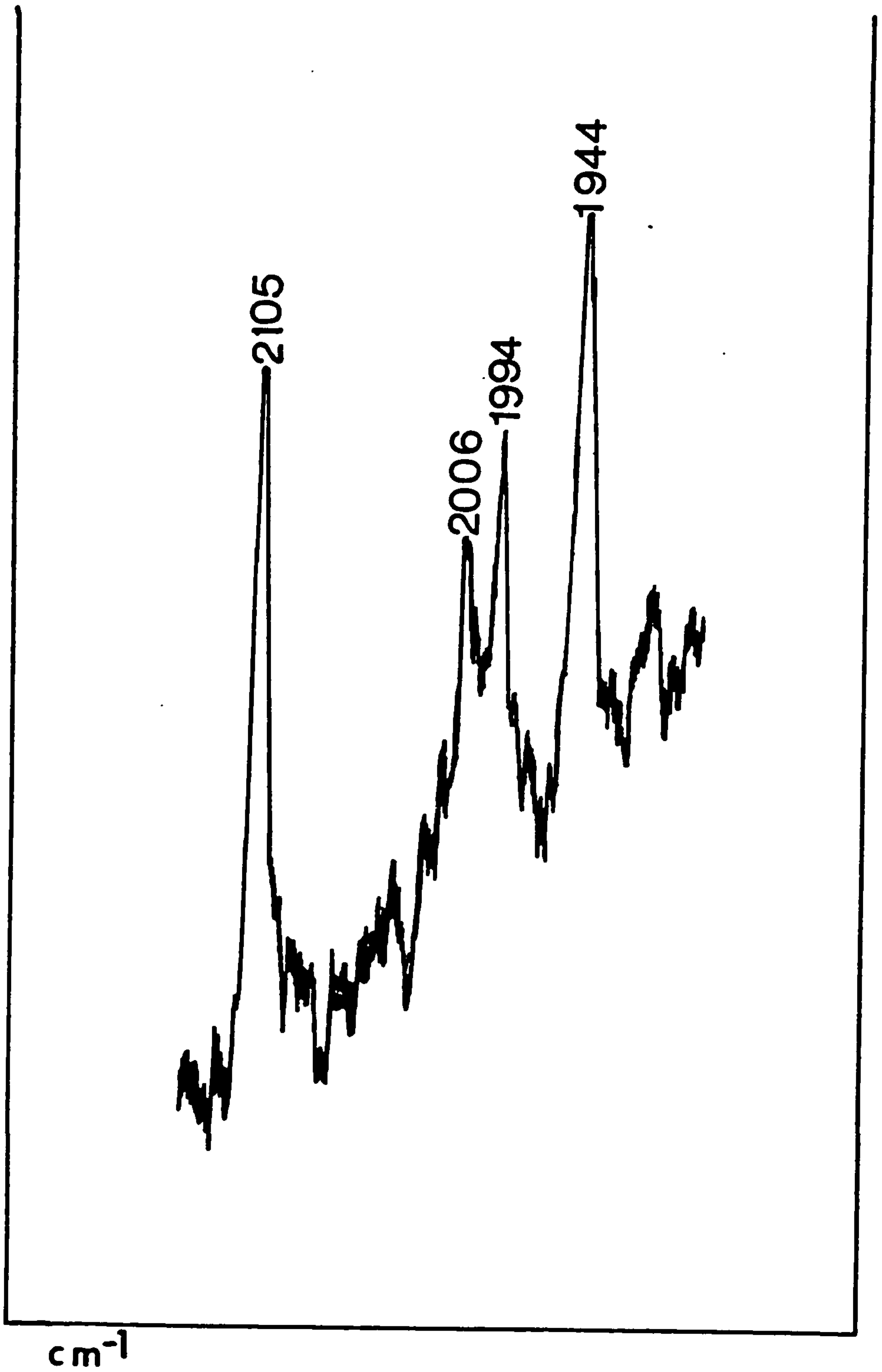

Figure 6.-Raman spectrum of $[Mn(CO)_4Br]_2$ (solid) in the CO stretching region.

TABLE VIII. VIBRATIONAL SPECTRA OF $[Mn(CO)_4X]_2$ (X = Br, I) (cm^{-1})

		ν(CO)				δ(MnCO) and ν(MnC)				ν(MnX)
$[Mn(CO)_4Br]_2$	i.r.(solid)	2103m	2089w	2048s,br	2037s	658s	632s	610s	603s	
		2030s	2020s	2012vs	2001m,sh	565vw	545w	465vw	419s	
		1982s	1958s,sh	1951s		410s,br				
	i.r.(solid)[a]					657vs	631vs	627sh	606vs	216vs
						600vs	563s	543s	472	186s
						466m	420vs	406vs	403sh	
						397sh	384			
	i.r.(CCl_4)[b]	2099m	2042vs	2011m	1975s					
	Raman(solid)	2117s	2015m	2000m	1953s	570w				202vvs
$[Mn(CO)_4I]_2$	i.r.(solid)	2100w	2089s	2065vw	2039s	654s	631s	612s	607s	
		2027s	2018s	2012vs	2007s	565vw	543w	467vw	435s	
		2000m,sh				410m				
	i.r.(solid)[a]					661sh	652vs	629vs	625sh	188s
						608vs	602vs	561	541s	166m
						474	468m	434vs	410vs	
						405sh	390			
	i.r.(CCl_4)[b]	2087w	2033vs	2009m	1976s					
	Raman(solid)	2015s	2006m	1994m	1944s	600w	473s	455m,sh	391m	185vvs

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[a] Data from ref. 93

[b] Data from ref. 92

in the CO frequencies, the vastly different scattering properties of the two compounds and the high intensity of all the lines in the $Mn(CO)_5Br$ spectrum would have been enough to rule out the possibility of any dimer formation.

From the above discussion, it appears that there was some correlation splitting in the solid-state spectra of the $Mn(CO)_5X$ derivatives but that it was restricted to the CO stretching region. Owing to this fortunate turn of events, the low-frequency vibrational spectra of the halopentacarbonylmetal complexes can be discussed in terms of the C_{4v} symmetry of an isolated $Mn(CO)_5X$ molecule.

i. Low-frequency Vibrations of the $Mn(CO)_5X$ Molecules

On the basis of C_{4v} symmetry, the fundamentals expected for the $Mn(CO)_5X$ molecules in the region below $700cm^{-1}$ are calculated by the method of Wilson, Decius, and Cross[102] to be: MnCO bending ($\underline{a}_1 + \underline{a}_2 + \underline{b}_1 + \underline{b}_2 + 3\underline{e}$), MnC stretching ($2\underline{a}_1 + \underline{b}_1 + \underline{e}$), MnX stretching ($\underline{a}_1$), CMnC bending ($\underline{a}_1 + \underline{b}_1 + \underline{b}_2 + 2\underline{e}$), and CMnX bending ($\underline{e}$). The $\underline{a}_1$ and $\underline{e}$ modes are the only i.r. active ones, whereas all but the $\underline{a}_2$ MnCO bending mode are Raman active. Most of the assignments of the low-frequency fundamentals are in agreement with those from other studies but enough differences exist for these to be discussed in full. The complete spectral data used in the assignments are shown in Table VI, and are illustrated by sample spectra in Figures 4,5,7,8, and 9.

Before discussing the bands below $150cm^{-1}$ it should be emphasized that the assignments for these frequencies are particularly

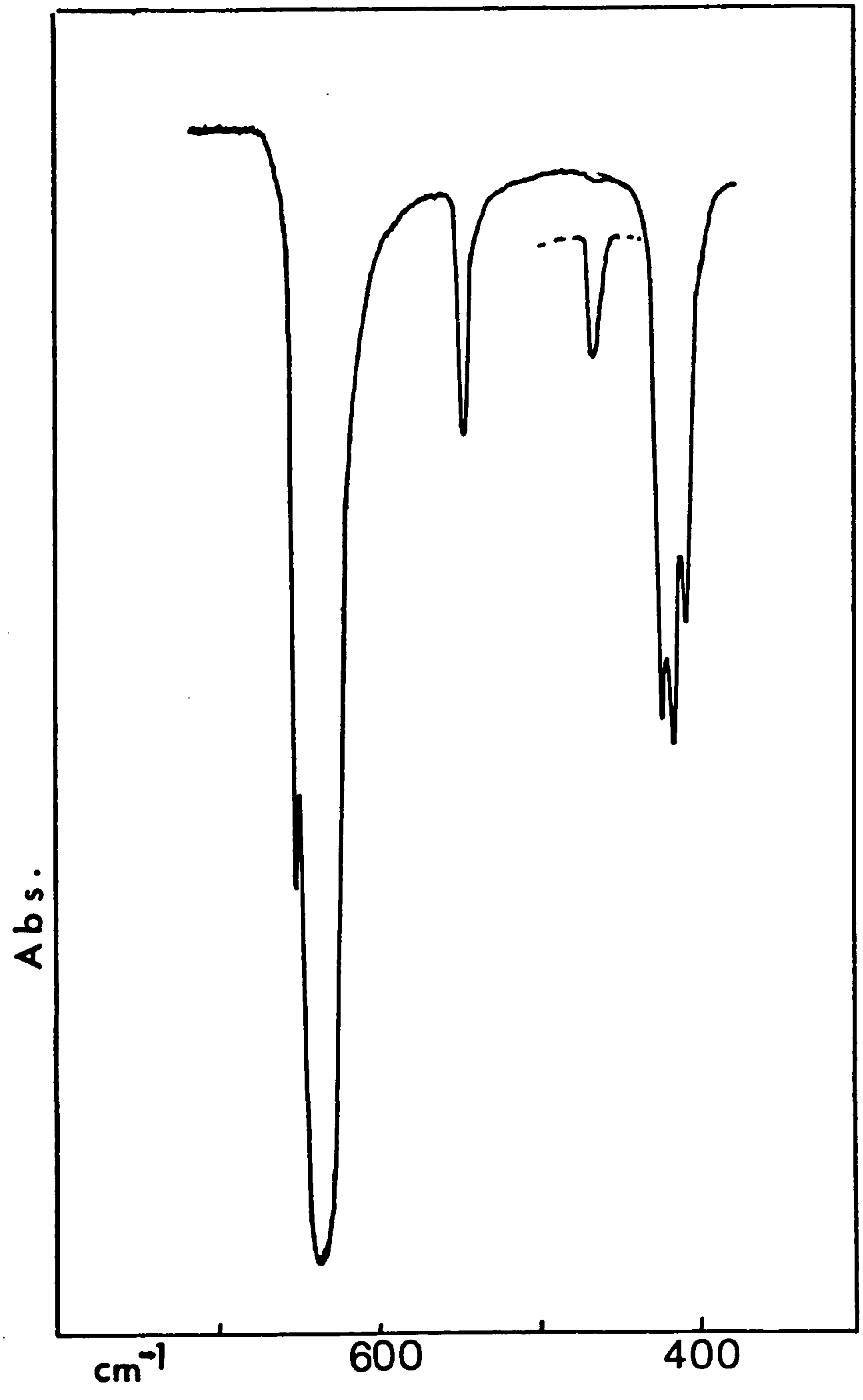


Figure 7.-Infrared spectrum of $Mn(CO)_5Br$ (nujol mull) in the 700-350cm^{-1} region.

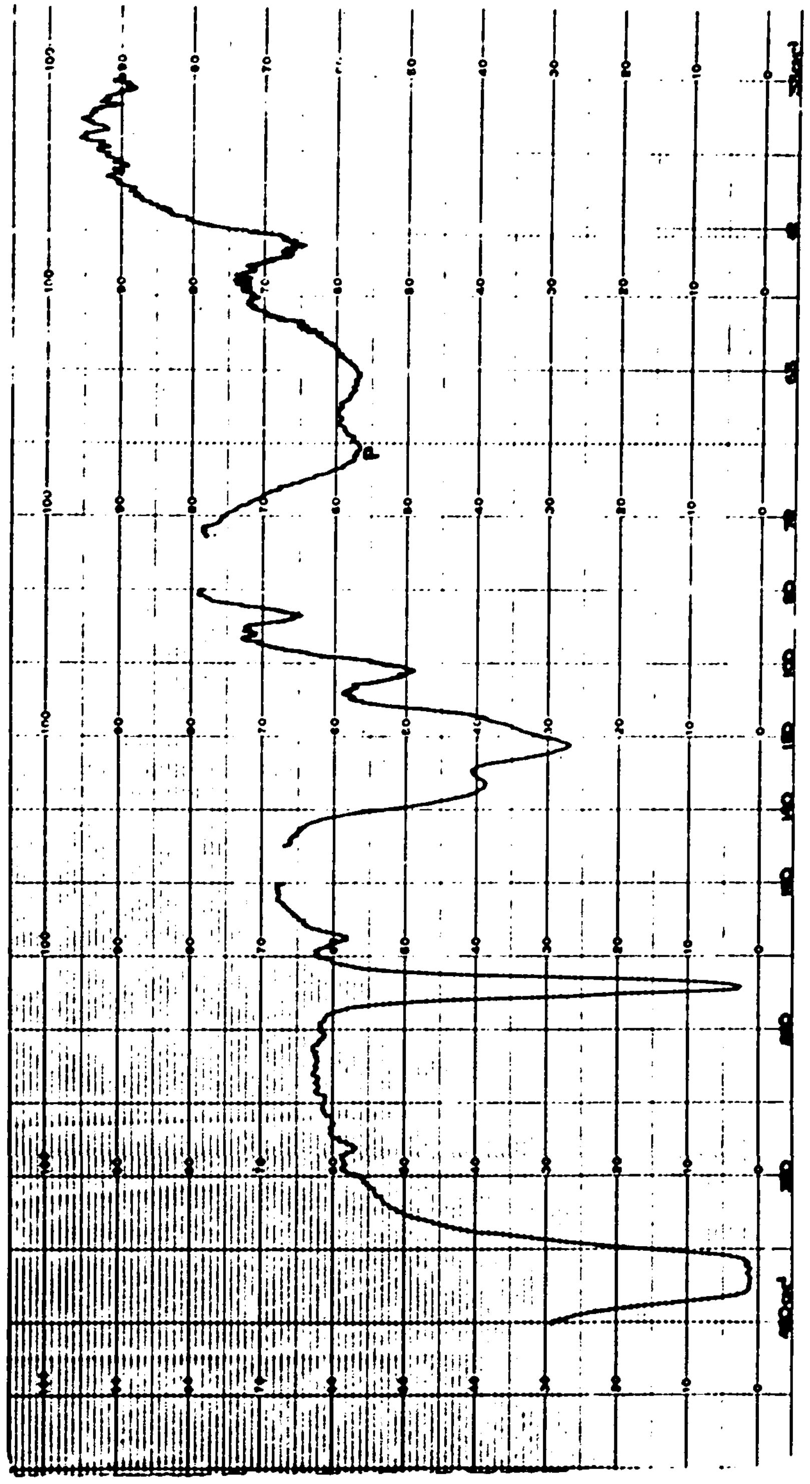


Figure 8.-Infrared spectrum of $Mn(CO)_5Br$ (nujol mull) below $450cm^{-1}$.

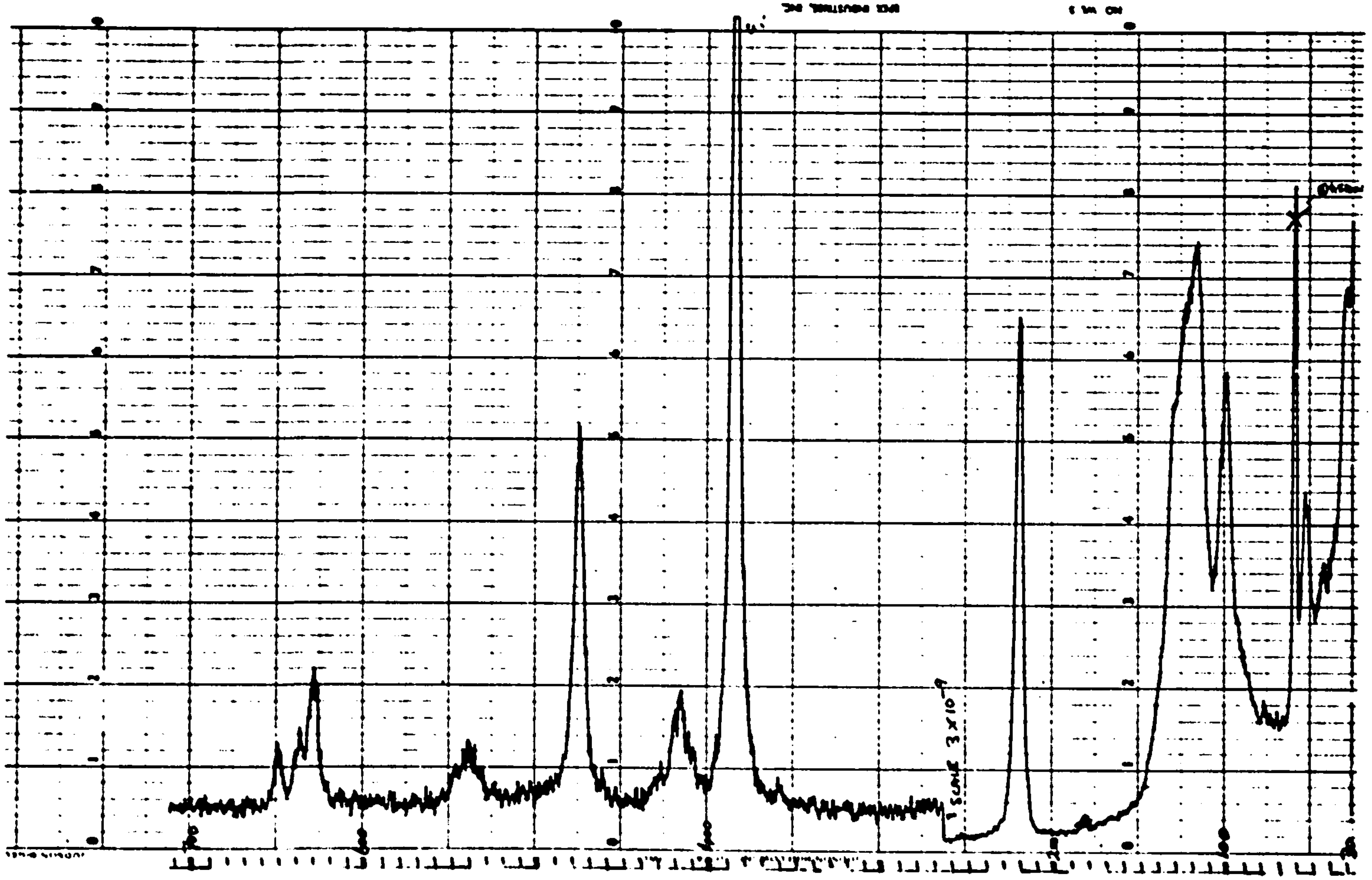


Figure 9.-Raman spectrum of $Mn(CO)_5Br$ (solid) below $700cm^{-1}$.

suspect owing to the likelihood of external modes of the solids becoming active in this region. Some of the external modes might also be coupled with each other, as well as with some of the very low-frequency internal modes. Furthermore, the three doubly degenerate vibrations [2δ(CMnC) + δ(CMnX)] may also interact with one another making the interpretation of the region below $150cm^{-1}$ even more speculative.

There is a weak band at $50cm^{-1}$ in the i.r. spectrum of $Mn(CO)_5Br$ and a medium intensity Raman line at $54cm^{-1}$. Neither of these frequencies have been reported before and they are tentatively both assigned to the CMnBr bending e mode, which is expected to occur below $70cm^{-1}$.[72] This mode is almost certainly the lowest fundamental frequency of the $Mn(CO)_5Br$ molecule and is expected to be extensively mixed with the two CMnC bending e modes. Hyams and Lippincott[88] recently reported bands at $50cm^{-1}$ and $53cm^{-1}$ in the i.r. and Raman spectra, respectively, of the bromide. They assigned the former and the Raman band at $45cm^{-1}$ to the δ(BrMnC) e mode, the Raman band at $53cm^{-1}$ being attributed to a b_1 CMnC bend.

There is a weak band at $64cm^{-1}$ in the i.r. spectrum of $Mn(CO)_5Br$, which had previously been observed by Edgell and Cengel[94] and by Valenti *et al.*[87] The former group had assigned it to the a_1 CMnC bending mode. It might have been possible to provide some support for their assignment if a strong Raman line had appeared at the same frequency, but fortunately the presence of an intense laser line at $65cm^{-1}$ prevented us from making measurements at this frequency. The i.r. band can also be explained either by one of the two i.r. inactive CMnC bending modes (b_1 or b_2), becoming active because of site symmetry effects, or by one of the six i.r. active external modes of the $Mn(CO)_5Br$ lattice. Hyams and Lippincott[88] report a shoulder on the Rayleigh line at 60 and 57cm^{-1} for $Mn(CO)_5Cl$ and $Mn(CO)_5I$, respectively, and assign these bands and the band at 53cm^{-1} mentioned above for $Mn(CO)_5Br$ to the $\underline{b}_1$ δ(CMnC) mode by comparison with the band at 57cm^{-1} for $Re(CO)_5I$ previously assigned as a $\underline{b}_1$ δ(CReC) mode.[70]

The two highest frequencies lying below 150cm^{-1} are assigned to the degenerate $\underline{e}$ δ(CMnC) fundamentals, whereas the band between 100-107cm^{-1} is assigned to the symmetric bending vibration expected. Adams and Squire[71] gave the same assignments to these modes, whereas Hyams and Lippincott[88] although giving the same assignments to the higher frequencies, assigned the bands they observed at 101, 98, and 98cm^{-1} in the Raman spectra of the chloride, bromide, and iodide, respectively, to the $\underline{b}_2$ CMnC bending mode.

There is no disagreement in the assignment of the metal-halogen stretching vibrations since these shift markedly on change of halogen. These bands are found at about 290, 220, and 190cm^{-1}, respectively, for the chloride, bromide, and iodide.

The four MnC stretching modes ($2\underline{a}_1 + \underline{b}_1 + \underline{e}$) are expected in the region 500-300cm^{-1} while the seven MnCO bending modes ($\underline{a}_1 + \underline{a}_2 + \underline{b}_1 + \underline{b}_2 + 3\underline{e}$) should lie in the region 700-450cm^{-1}. Owing to the proximity of the two regions, extensive mixing of the modes of the same symmetry type is anticipated. The assignments for these modes differ somewhat from those presented by the other investigators.

The strongest i.r. active MnC stretching vibration of $Mn(CO)_5Br$ was at approximately 420cm^{-1}. Under high resolution this band appeared as a doublet. The splitting could have been the result of (1) factor group effects on one of the $\underline{a}_1$ modes or on the $\underline{b}_1$ mode: both of these non-degenerate species would give rise to two i.r. active modes ($\underline{b}_{1u}$ + $\underline{b}_{3u}$) in the crystal or (2) site symmetry effects on the degenerate $\underline{e}$ mode which would also have led to two i.r. active modes ($\underline{a}'$ + $\underline{a}''$) in the crystal. By analogy with the CO stretching region, the most intense band in the MnC stretching region would be expected to result from the $\underline{e}$ mode, and as a consequence, the formation of the doublet is attributed to the second possibility above. The $\underline{e}$ mode should also be Raman active. A medium intensity line was found at 415cm^{-1} but no splitting could be detected in this case. It will be demonstrated shortly that the assignment proposed for the $\underline{e}$ mode can be verified from overtone and combination spectra. The strong i.r. bands at 418 and 427cm^{-1} for $Mn(CO)_5Cl$ and $Mn(CO)_5I$, respectively, have been similarly designated as MnC stretching $\underline{e}$ modes. The assignments given are in agreement with those proposed by other research groups.[71,72,94]

Each pentacarbonyl derivative exhibited a strong Raman line in the neighbourhood of 385cm^{-1}, but only in the case of $Mn(CO)_5I$ was there a corresponding i.r. band, and even then, it was extremely weak. These frequencies have been assigned to the $\underline{a}_1$ (radial) MnC stretching modes, which, by analogy with the $\underline{a}_1$ (radial) CO stretching modes, would be expected to exhibit strong Raman lines and weak i.r. bands, in accord with the experimental observations. The assignment is substantiated by the polarization data of Adams and Squire,[71] and recently by that of Hyams and Lippincott.[88]

There was a fairly strong band near 410cm^{-1} in the i.r. spectrum of each compound. [In the case of $Mn(CO)_5Cl$, the band near

409cm^{-1} was in fact the strongest in the MnC stretching region which prompted Adams and Squire[71] to assign this band to the ν(MnC) e mode. However, the overtone and combination spectra were better explained if it was assigned to the $\underline{a}_1$ (axial) mode and the somewhat weaker band at 418cm^{-1} was assigned to the e mode.] These bands had previously been reported as shoulders but in the spectra in this study they were quite well resolved, especially in the case of $Mn(CO)_5I$. There were weak Raman lines coincident with the i.r. bands. With the exception of the work of Clark and Crosse[72] and more recently that of Hyams and Lippincott,[88] these frequencies have been completely disregarded in all previous assignments of the MnC stretching modes. Clark and Crosse studied the i.r. spectra in tetrachloroethylene solution and indicated that the bands near 410cm^{-1} most probably arose from $\underline{a}_1$ MnC stretching modes, but they did not suggest which type (*i.e.* axial or radial). In this work these frequencies are assigned to the $\underline{a}_1$ (axial) modes. If this designation is correct, then the Raman lines should be polarized. Unfortunately, the lines were too weak for polarization measurements. The proposed assignment of the $\underline{a}_1$ (axial) modes is contrary to that of Adams and Squire,[71] Edgell and Cengel,[94] and Hyams and Lippincott[88] who assigned these modes to the frequencies observed near 470cm^{-1}. However, it is felt that the i.r. bands at 470cm^{-1} are much too weak compared with those at 410cm^{-1} to support their assignment. In the present study, the former have been assigned to the $\underline{a}_1$ MnCO bending modes. This assignment is in harmony with the solution Raman work of Adams and Squire[71] who found that the lines at 470cm^{-1} were polarized. Hyams and Lippincott[88] have surprisingly assigned the $\underline{b}_1$ ν(MnC) mode to around 420cm^{-1} for all three complexes.

In fact they assigned all the bands between 426-400cm^{-1} to 2$\underline{e}$ [ν(MnC) + δ(MnCO)] + $\underline{b}_1$ [ν(MnC)].

A weak Raman line was observed near 630cm^{-1} for both $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ but not for $Mn(CO)_5I$. These lines have previously been noted by Edgell and Cengel,[94] Adams and Squire,[71] and recently by Hyams and Lippincott.[88] The first two research groups assigned the frequencies to the $\underline{a}_1$ and one of the $\underline{e}$ MnCO bending modes, respectively. However, both of these assignments necessitate the appearance of an i.r. band for each compound in the region of 630cm^{-1}, and since these were not observed, the assignment of the frequencies to either the $\underline{b}_1$ or the $\underline{b}_2$ purely Raman active MnCO bending modes is preferred. Hyams and Lippincott[88] attributed these bands to the Raman counterpart of the strong i.r. MnCO bends of $\underline{e}$ symmetry observed near 640cm^{-1}.

The very strong band near 640cm^{-1}, the strong shoulder near 650cm^{-1}, and the medium band near 550cm^{-1} have all been assigned to δ(MnCO) $\underline{e}$ modes, since we expect only four ($\underline{a}_1$ + 3$\underline{e}$) MnCO bending modes in the infrared and the symmetric $\underline{a}_1$ bending mode has already been assigned. This is in agreement with Adams and Squire's assignment[71] but conflicts with that recently proposed by Hyams and Lippincott.[88] The latter, while assigning the bands near 640 and 550cm^{-1} to $\underline{e}$ δ(MnCO) modes, preferred to assign the strong shoulder near 650cm^{-1} to the $\underline{a}_1$ δ(MnCO) vibration. The third δ(MnCO) doubly degenerate vibration was then assigned to bands in the 420-410cm^{-1} region.

One unusual feature of the CS_2 solution i.r. spectrum of $Mn(CO)_5I$ was the appearance of a weak band at 608cm^{-1}, which was *not* observed in the solid-state spectrum. Reference to the literature shows that a similar band appears in tetracholoroethane,[72] cyclohexane,[20,94] and carbon tetrachloride[20,94] solutions. We are unable to offer an explanation for this anomaly, although Hyams and Lippincott[88] assigned this band, by comparison with a weak Raman band in $Re(CO)_5I$ to a $\underline{b}_2$ MnCO bending mode. If the bands had appeared in the solid but not in solution, then this assignment would be acceptable; in the existing situation, however, it seems an unlikely one.

In conclusion, it should be re-emphasized that because modes of the same symmetry type are known to be extensively in the low-frequency region, none of the frequencies in this region will be comprised of the assigned motion alone. This caveat applies particularly to the $\underline{a}_1$ and $\underline{e}$ modes in the MnC and MnCO bending region.

ii. Overtone and Combination Spectra of the $Mn(CO)_5X$ Molecules in the 1350-700 and 2800-2250cm^{-1} Regions.

The selection rules for the binary combinations of the $Mn(CO)_5X$ molecules assuming C_{4v} symmetry are shown in Table IX. It is evident that i.r. inactive modes ($\underline{a}_2$, $\underline{b}_1$, and $\underline{b}_2$) must combine with $\underline{e}$ modes in order to produce i.r. allowed combinations. This point is important in some of the low-frequency assignments to be discussed shortly. All first overtones are allowed, but are expected to be only weakly i.r. active. The frequencies observed in the 1350-700 and 2800-2250cm^{-1} regions and the proposed assignments are given in Table VI . In order to facilitate the interpretation of the assignments, a table containing

TABLE IX. SELECTION RULES FOR BINARY COMBINATIONS UNDER C_{4v} SYMMETRY.[a,b]

	$\underline{a}_1$	$\underline{a}_2$	$\underline{b}_1$	$\underline{b}_2$	$\underline{e}$
$\underline{a}_1$	A_1	A_2	B_1	B_2	E
$\underline{a}_2$		A_1	B_2	B_1	E
$\underline{b}_1$			A_1	A_2	E
$\underline{b}_2$				A_1	E
$\underline{e}$					$A_1 + A_2 + B_1 + B_2$

[a] The activities are: $\underline{a}_1$, $\underline{e}$, i.r. allowed; $\underline{a}_1$, $\underline{b}_1$, $\underline{b}_2$, $\underline{e}$, Raman allowed.

[b] For $\underline{e}^2$ the symmetry species is $A_1 + B_1 + B_2$.

frequency information for only the fundamentals is provided (Table X). Typical spectra in the 1350-700 and 2800-2250cm^{-1} regions are shown in Figures 10 and 11 respectively.

In the discussion of the low-frequency vibrations, the MnC stretching e modes were assigned to the frequencies observed near 420cm^{-1}. The non-appearance of the first overtones, although these modes apparently combine with the other MnC stretching fundamentals to produce fairly strong combinations, provides some support for this assignment. A more important observation, however, is that the combination bands near 2500cm^{-1} can *only* be satisfactorily explained by the combination of the bands near 420cm^{-1} with the i.r. inactive b_1 CO stretching modes at approximately 2080cm^{-1}. It could perhaps be argued that forbidden combination bands may have become active because of solid-state effects, but the intensity of these combination bands as well as the appearance of a similar band for $Mn(CO)_5I$ in CS_2 solution, make this possibility somewhat remote. Consequently, in order for the combination bands at 2500cm^{-1} to satisfy the selection rules, the i.r. bands at 420cm^{-1} *must* be of e symmetry.

It is also possible to verify the assignment of some of the other low-frequency e modes from studies of the combination spectra in the 2800-2250cm^{-1} region and knowledge of the b_1 CO stretching modes from Raman spectra. For example, all three compounds exhibit low-intensity combination bands at about 2720cm^{-1} which are best explained as arising from combinations of the b_1 CO stretching modes with the MnCO bending modes at about 640cm^{-1}. The activity of the combination bands suggests that the MnCO bending modes are of e symmetry, in accord with the previous

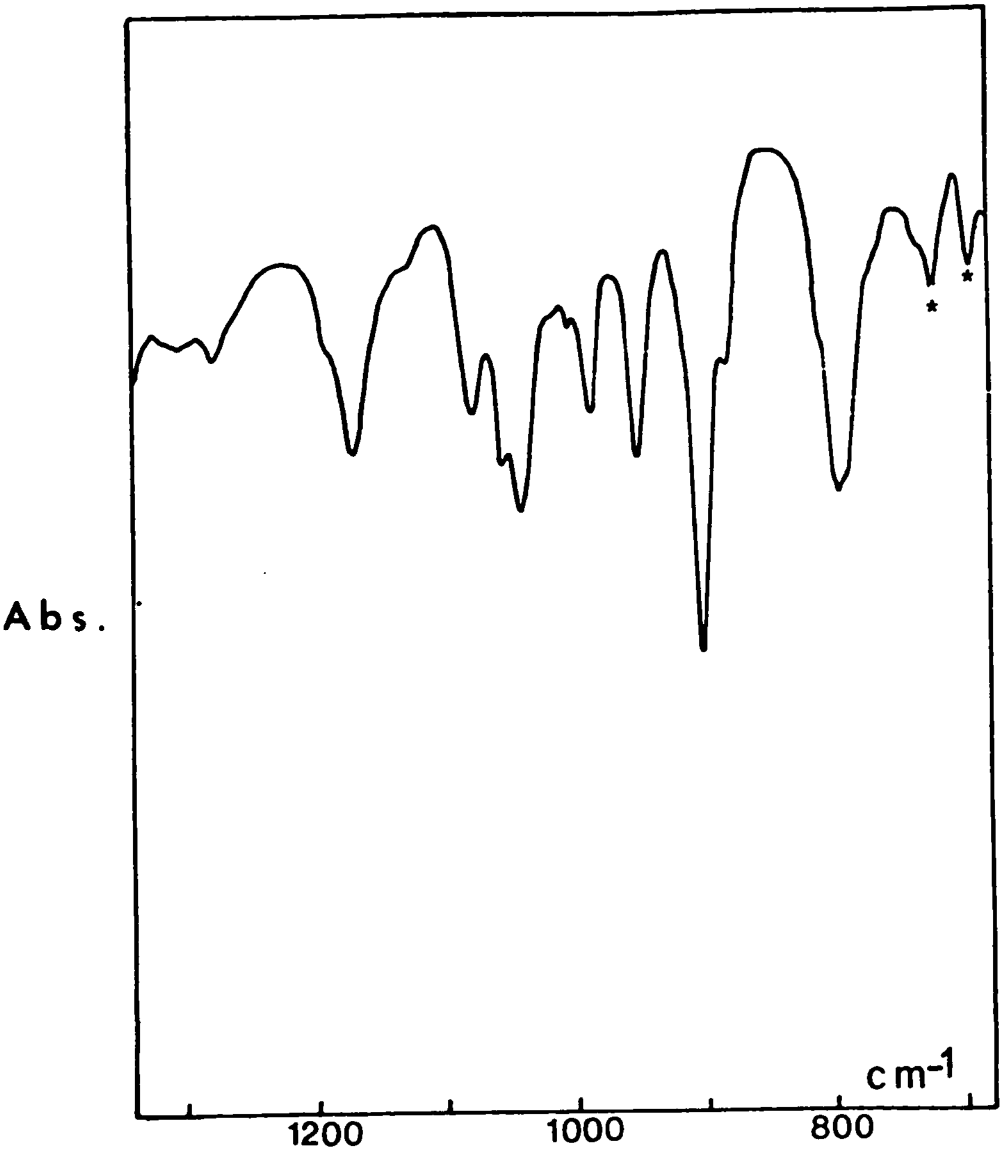


Figure 10.-Overtone and combination spectrum of $Mn(CO)_5Br$ (nujol mull) in the 1350-700cm^{-1} region (bands marked * are nujol peaks).

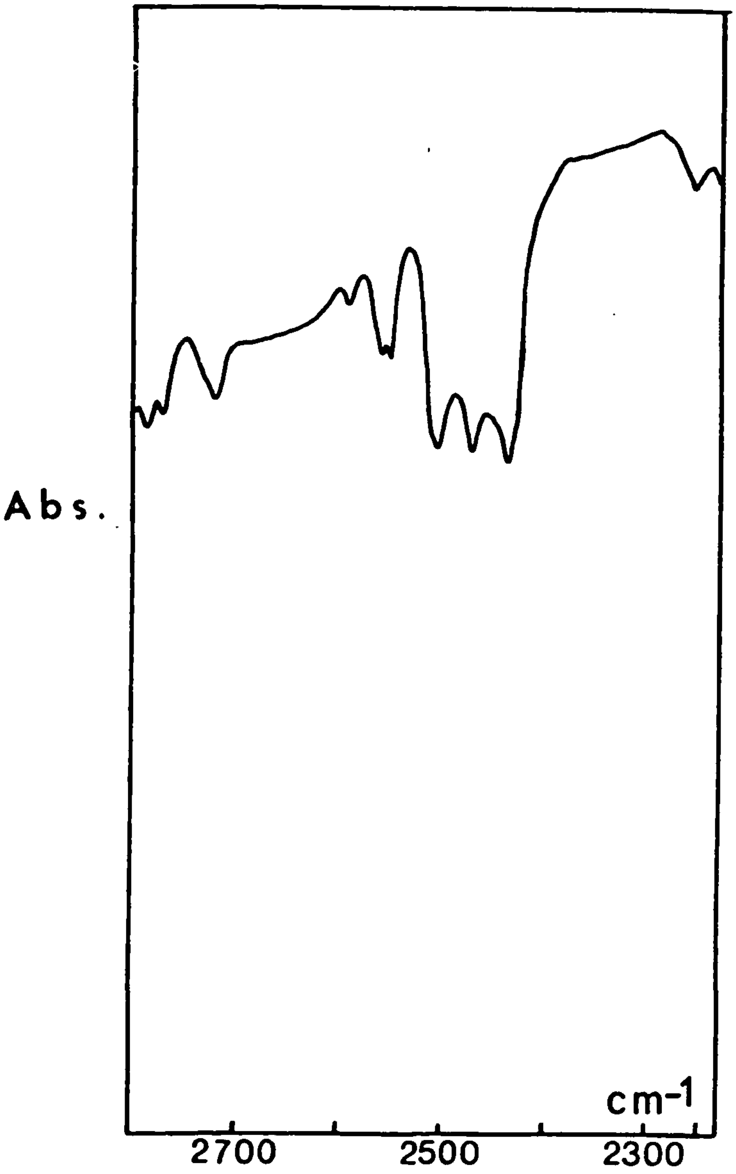


Figure 11.-Combination spectrum of $Mn(CO)_5Br$ (nujol mull) in the 2800-2250cm^{-1} region.

TABLE X. FUNDAMENTAL MODES OF THE $Mn(CO)_5X$ MOLECULES USED IN THE ASSIGNMENT OF THE OVERTONE AND COMBINATION SPECTRA.[a]

i in ν_i	Symmetry	Approx. Description	Frequency (cm^{-1}) X = Cl	X = Br	X = I[b]	
1	a_1	CO radial str.	2144	2139	2132	(2127)
2	a_1	CO axial str.	1994	1997	2002	(2005)
3	a_1	MnCO	478	471	467	(464)
4	a_1	MnC axial str.	409	408	406	(410)[c]
5	a_1	MnC radial str.	382	385	386	
8	a_2	MnCO bend	535[d]	533[d]	518[d]	(520)[d]
9	b_1	CO str.	2080	2075	2070	(2080)[e]
10	b_1	MnCO bend	570[d]	568[d]	563[d]	(569)[d]
11	b_1	MnC str.	350[d]	348[d]	352[d]	(359)[d]
13	b_2	MnCO bend	628	630	625[d]	
15	e	CO str.	2050	2049	2043	(2045)
16	e	MnCO bend	654	651	652	(651)
17	e	MnCO bend	638	638	638	(641)
18	e	MnCO bend	550	547	544	(547)
19	e	MnC str.	418	418	427	(431)

[a] Some of the fundamentals in the solid-state spectra were split by correlation effects. Consequently, whenever this occurred the frequency shown in the table is the mean of the observed frequencies. For those fundamentals where both i.r. and Raman data were available, the frequencies given in the table are from the i.r. spectra

[b] The values shown in parentheses are for the CS_2 solution i.r. spectrum. In those cases where solution data were not available the frequencies from the solid-state spectrum were used.

[c] In *n*-hexane solution.

[d] Predicted from combination spectra

[e] From ref. 99

assignments.[71,72,94]

A few of the bands in the combination spectra can only be explained by the combination of e fundamentals with low-frequency fundamentals which were not observed in either the i.r. or Raman spectra. For example, the relatively strong bands at 988, 986, and $990cm^{-1}$ in $Mn(CO)_5Cl$, $Mn(CO)_5Br$, and $Mn(CO)_5I$, respectively, can only be explained as either the combination of the $\nu(MC)$ e vibration with an MnCO mode close to $570cm^{-1}$ or the combination of a $\delta(MnCO)$ e mode (probably the strongest near $640cm^{-1}$) with a $\nu(MnC)$ vibration near $350cm^{-1}$. The predicted frequencies along with the suggested assignments are given in footnotes e and f of Table VI. The assignments cannot at present be substantiated further.

It is also worth pointing out a few very weak bands that were observed in the CS_2 solution spectrum of $Mn(CO)_5I$ at 695, 713, and $730cm^{-1}$. These bands are explained as combinations between the strongest $\delta(MnCO)$ e mode at $640cm^{-1}$ and low-lying vibrations at 54,72, and $89cm^{-1}$, respectively. Alternatively, if the $651cm^{-1}$ e mode is used, fundamental frequencies at 64, 82, and $99cm^{-1}$, respectively, would be predicted.

iii. Vibrational Spectra of $[Mn(CO)_4Br]_2$ and $[Mn(CO)_4I]_2$

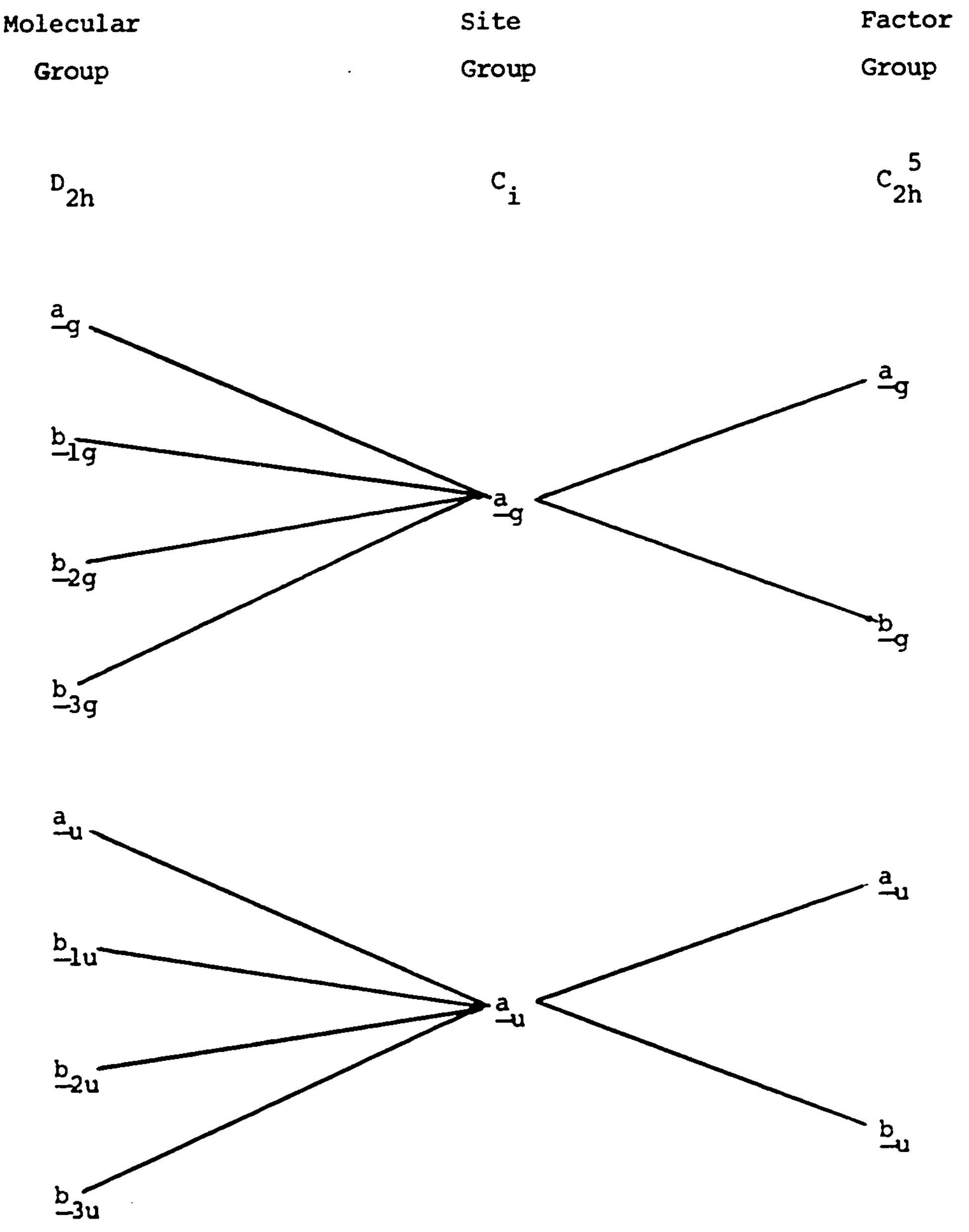
It has already been mentioned that the solid-state i.r. and laser Raman spectra of $[Mn(CO)_4Br]_2$ and $[Mn(CO)_4I]_2$ in the CO stretching and low-frequency regions were recorded in the present work. These spectra are commented on briefly below.

The solution i.r. spectra of the three $[Mn(CO)_4X]_2$ derivatives have been thoroughly investigated in the CO stretching region by El-Sayed and Kaesz[92] and Abel and Butler.[103] As mentioned already (p. 30) the solid-state i.r. spectra of these complexes in the low-frequency region have also received some attention. The data from this study for the solid-state i.r. and laser Raman spectra of $[Mn(CO)_4Br]_2$ and $[Mn(CO)_4I]_2$ in the CO stretching and low-frequency regions are presented in Table VIII. The CCl_4 solution and solid-state i.r. data of El-Sayed and Kaesz,[92] and the solid-state i.r. data of Sartorelli, Valenti and Zingales[93] are also given in the table.

The crystal and molecular structure of $[Mn(CO)_4Br]_2$ has been determined.[104] The space group symmetry is $P2_1/c$ (C_{2h}^5) and there are four dimeric molecules per unit cell. The site symmetry is C_i. The molecular structure (Figure 12) consists of discrete dimeric molecules formed by two octahedra joined at a common edge with bridging bromine atoms equally shared between the manganese atoms. Within experimental error, each molecular unit is of D_{2h} symmetry. $[Mn(CO)_4I]_2$ is presumably isomorphous with $[Mn(CO)_4Br]_2$.

A group theoretical analysis for the D_{2h} structures leads to the prediction of four i.r. active ($\underline{b}_{1u} + \underline{b}_{2u} + 2\underline{b}_{3u}$) and four Raman active ($2\underline{a}_g + \underline{b}_{1g} + \underline{b}_{2g}$) CO stretching modes. A factor group analysis

TABLE XI. FACTOR GROUP ANALYSIS FOR $[Mn(CO)_4X]_2$ SPECIES.[a,b]



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[a] All the "g" modes are Raman active and, apart from a_u, all the "u" modes are infrared active.

[b] For the correlation between D_{2h} and C_i, $C_{2h}(z)$ was used.

shown in Table XI indicates that every one of these CO modes could be split into two components in the crystal. For example, the i.r. active $\underline{b}_{1u}$ mode could be split into the two i.r. active modes $(\underline{a}_u + \underline{b}_u)$.

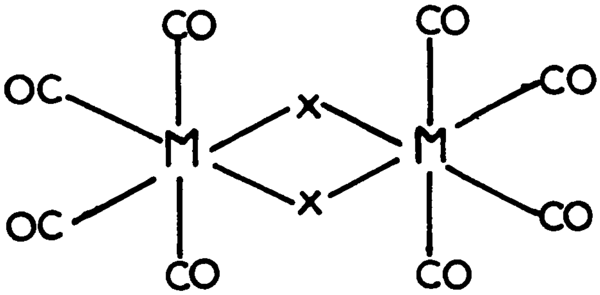

Figure 12.-Structure of $[Mn(CO)_4X]_2$.[104]

Splittings such as this would, in part, explain the complexity of the solid-state i.r. spectra of the dimers in the CO stretching region when compared to the spectra in CCl_4 solution. The appearance of a number of weak bands, presumably attributable to ^{13}C-satellites, further complicates the solid-state i.r. spectra.

In sharp contrast to the infrared spectra, the solid-state Raman spectra in the CO stretching region proved remarkably simple. Even though the dimers were extremely poor scatterers, four sharp lines were easily observable in both cases (Figure 6), in agreement with the group theoretical prediction for D_{2h} symmetry. There were no splittings detected in any of the lines. Although it is not strictly valid to compare frequencies from different physical states, it is apparent that there are no coincidences between the CCl_4 solution i.r. and the solid-state Raman data. The complexity of the solid-state i.r. spectra in the CO stretching region renders a similar comparison less meaningful. However, even though fewer Raman lines were observed in the low-frequency than were expected, especially in the case of $[Mn(CO)_4Br]_2$, it is possible to compare the solid-state i.r. and Raman data in this region. There are again no coincidences found in the spectra recorded in this work though a few coincidences do exist with the i.r. bands reported by Sartorelli, Valenti, and Zingales.[93] The appearance of four CO lines in the Raman spectra and the lack of any appreciable number of coincidences between the i.r. and Raman spectra is in accord with centrosymmetric D_{2h} structures for the dimers.

The most intense lines in the Raman spectra of $[Mn(CO)_4Br]_2$ and $[Mn(CO)_4I]_2$ appeared at 202 and 185cm^{-1}, respectively. These lines are readily assigned as MnBr and MnI stretching vibrations.

C. EXPERIMENTAL

i. Materials

The compounds studied were prepared by the methods described in the literature: $Mn(CO)_5Cl$ and $Mn(CO)_5Br$;[97] $Mn(CO)_5I$;[105] $[Mn(CO)_4Br]_2$ and $[Mn(CO)_4I]_2$.[97] The purity of the compounds was established by the absence of any impurity bands in their i.r. spectra in the CO stretching region.

ii. Spectra

All spectra were recorded using freshly prepared samples.

I.r. spectra below $300cm^{-1}$ were recorded on a Beckman IR-11 spectrophotometer. In the other regions spectra were recorded on a Perkin Elmer model 521 spectrophotometer. All measurements were carried out at room temperature with the samples in the form of Nujol mulls pressed between plates appropriate for the spectral region under investigation The solution spectrum of $Mn(CO)_5I$ was studied using spectrograde CS_2. The frequencies shown in the tables are accurate to ± $1cm^{-1}$.

Raman spectra of the powdered solids were recorded on either a Spex Ramalog or a Jarrell-Ash model 25-300 Raman spectrophotometer using helium-neon (6328 Å) excitation. The frequencies shown in the tables are accurate to ± $1\text{-}2cm^{-1}$.

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PART II

THE INFRARED SPECTRA OF ISOTOPICALLY SUBSTITUTED METAL CARBONYLS

I. ^{13}CO-SUBSTITUTED *cis*-$Fe(CO)_4I_2$ AND *cis*-$Fe(CO)_4Br_2$

II. $C^{18}O$-SUBSTITUTED *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$)

CHAPTER I INTRODUCTION

In the past decade isotopic carbonyl exchange reactions with metal carbonyls have been the subject of numerous studies. These studies may be classified into two general groups according to which isotopes are used: (1) Studies employing the radioactive ^{14}CO and (2) studies employing ^{13}CO or $C^{18}O$. The former are carried out by measuring changes in radioactivity, while the latter employ the more easily manageable infrared spectroscopic technique. The present account will be restricted to the spectroscopic investigations, although some ^{14}CO studies will be discussed, mainly for comparative purposes.

According to vibrational theory[1] the stretching force constant between two atoms is virtually unaffected by isotopic substitution. A change in mass of either or both atoms will cause a shift in the vibrational frequency. The carbonyl stretching fundamental frequencies are very amenable to isotopic exchange studies because, especially in non-polar solvents, the bands are found to be very sharp, and the frequency shifts arising from isotopic substitution are easily observable. The natural abundance of ^{13}C is $\sim$1.1%; therefore, it is possible to observe weak bands due to ^{13}CO even in unenriched samples, particularly with concentrated solutions.

There are several uses for the infrared spectroscopic studies of isotopically enriched carbonyls, or of carbonyls exhibiting naturally occurring isotopic bands.[2]

1. They may be used for the determination of the infrared-inactive CO stretching fundamentals of the all-^{12}CO molecules. Thus bands which

are forbidden, or inactive in the infrared spectra of the all-^{12}CO molecules may become active on lowering the symmetry of the molecule through isotopic substitution. It has been noted, in fact, that such stretching frequencies can be determined with a higher degree of accuracy than from Raman spectra or from studies of overtone and combination regions.[2]

2. Comparisons may be made of the observed and calculated spectra of the all-^{12}CO and isotopically substituted species in order to check the validity of the assignments and force constant calculations.

3. The isotopic data may be employed for force constant calculations. In most systems, the number of force constants exceeds the number of fundamental frequencies from which they must be calculated, with the result that a force field cannot be defined unless a number of empirical approximations are made. The isotopically substituted complexes thus provide additional bands to minimize, or totally eliminate, the necessity of these approximations.

4. Even without force constant calculations the number of isotopic bands, and their shifts from the parent modes, may be useful in the assignment of the fundamental frequencies without any prior assumptions being made.

5. The isotopic investigations may be utilized in the determination of the reaction mechanisms which involve CO uptake or insertion. The changes in intensity of the parent fundamentals, as well as of the isotopic bands, provide qualitative and sometimes quantitative data for the determination and comparison of the rates of CO exchange.

6. Isotopic exchange studies may also be used for the refined

interpretation of absolute infrared intensity data. This becomes possible from a study of the calculated force constants and the associated eigenvectors.

Apart from a few exceptions, the force constant calculations mentioned above were carried out by using simplified force fields which only took account of the CO stretching fundamentals. The validity of these calculations has been questioned by a number of authors. The arguments for and against such calculations will therefore be discussed in Chapter III.

The various isotopic exchange reactions that have been carried out with transition metal carbonyl complexes, as well as, the infrared spectroscopic studies accompanying them will be reviewed in Chapter II. As an extension of these studies, an investigation has been made on the isotopic exchange reactions for the two systems *cis*-$Fe(CO)_4X_2$ (X = Br,I) and *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$). The results are presented and discussed in Chapters IV and V, respectively.

CHAPTER II REVIEW OF INFRARED STUDIES ON ISOTOPICALLY SUBSTITUTED METAL CARBONYL COMPLEXES

A. GROUP VIB

i. Binary Carbonyl Complexes

The exchange reactions of ^{14}CO with the complexes $M(CO)_6$ (M = Cr,[3] Mo,[4] W[5]) have been studied kinetically in the gas phase and found to be extremely slow. Thus, it is difficult to obtain spectroscopic data by direct exchange with ^{13}CO or $C^{18}O$.

Since it was reported by Kaesz, Winstein, and Kreiter[6] that under atmospheric pressure, CO substituted into $C_8H_{10}Mo(CO)_3$ (1,3,5-cyclooctatrienemolybdenum tricarbonyl) to give $Mo(CO)_6$ ultimately, the reaction was restudied by Harrill and Kaesz[7] using ^{13}CO. It was found that norbornadienemolybdenum tetracarbonyl, $C_7H_8Mo(CO)_4$, also exchanged, with the same end products being obtained. In this way Harrill and Kaesz were able to circumvent the problem of the very slow substitution of molybdenum hexacarbonyl. These authors reported four peaks for $Mo(CO)_6$ in the CO stretching region at 2108.7, 2009.3, 1988.4, and 1956.3cm^{-1}. The strong band at 1988.4cm^{-1} was immediately assigned to the only expected ^{12}CO mode (of $\underline{t}_{1u}$ symmetry), and the other three peaks of low-intensity were attributed to the mono-^{13}CO substituted derivative which would be present in 6% natural abundance. The di- and tri-^{13}CO substituted species' frequencies were obtained by keeping about 50mg of the appropriate olefin complex in 3ml of cyclohexane under an atmosphere of ^{13}CO for several days, removing the solvent under reduced pressure, and subliming the hexacarbonyl formed whose spectrum were then taken in cyclohexane.

The frequencies of the di- and tri-substituted species were back-calculated using force constants which were derived from the four bands mentioned above and were found to agree quite well with the observed values. For the di-^{13}CO species, both possible isomers, the *cis* and *trans*, were observed to be present indicating that the carbonyl groups in the original olefin complexes do not retain their stereochemistry during the olefin displacement. It is important to note that this conclusion could only be reached by observing that when the reaction of $C_7H_8Mo(CO)_4$ with ^{13}CO was stopped at an early stage, the unconverted olefin complex which was recovered exhibited only slight enrichment due to its own exchange.

Bor and Jung[2] have measured the CO stretching frequencies of the mono-^{13}CO derivative, $Mo(CO)_5(^{13}CO)$, by the enrichment of the ^{13}CO content of $Mo(CO)_6$ to 6-8%, and used them to calculate the CO stretching force constants. The latter were then used to calculate the inactive modes in the unsubstituted complex as well as the frequencies of all the possible substituted derivatives. Their calculated frequencies for the i.r. inactive modes of $Mo(CO)_6$ were slightly higher (1-2cm^{-1}) than those reported by Harrill and Kaesz.[32] Bor and Jung[2] also dealt with the vibrational eigenvectors which are important from the point of view of band intensity considerations, as well as, for the determination of the dipole moment gradients.

Jones, McDowell, and Goldblatt[8] have performed an exhaustive study of isotopically substituted Group VIB hexacarbonyls. They synthesized the enriched hexacarbonyls of chromium, molybdenum, and tungsten by standard high pressure techniques using the appropriate carbon monoxide gas

$^{12}C^{18}O$(99% ^{18}O) and $^{13}C^{16}O$(93% ^{13}C). The vibrational spectra of $M(^{12}C^{16}O)_6$, $M(^{13}C^{16}O)_6$, and $M(^{12}C^{18}O)_6$ could thus be observed directly. Infrared spectra were reported for the vapour phase, in CCl_4 solution for the chromium and molybdenum complexes, and in CS_2 solutions for the tungsten complexes. Raman spectra were reported for both the solution and solid phases of these species. From the results, most of the fundamental vibrations were assigned and force constants calculated for a general quadratic force field. Also a set of stretch-stretch interaction constants were presented by the authors which could be transferred, with discretion, to other metal carbonyls.

ii. Substituted Metal Carbonyl Complexes

The exchange reaction of $C^{18}O$ with *o*-phenanthrolinechromium tetracarbonyl, $Cr(CO)_4$ (*o*-phen), has been investigated by Dokiya, Johnston, and Basolo[9] in order to determine whether the stereochemically different CO ligands exchanged at different rates. They found by observing changes in the infrared spectrum, that the rate of exchange of the equatorial CO groups (those *trans* to the amine) was significantly smaller than that of the axial ligands. This difference was explained as arising from the fact that the π^* orbitals of the axial CO groups compete for the same set of metal d orbitals, whereas the equatorial CO groups are *trans* to an essentially non-π-bonding ligand, giving the Cr-CO bond to the equatorial CO groups a greater degree of π character.

B. GROUP VIIB

i. Binary Metal Carbonyl Complexes

Since it had been found that $Mn_2(CO)_{10}$[10,11] and $Re_2(CO)_{10}$[12] exchanged extremely slowly with radioactive carbon monoxide, it was therefore necessary to find another means than direct exchange to effect enrichment with isotopic CO. Harrill and Kaesz[13] found that $HRe_3(CO)_{14}$ reacted at 25° with CO at atmospheric pressure in cyclohexane to give $HRe(CO)_5$ and $Re_2(CO)_{10}$. The reaction with ^{13}CO was used therefore to determine the fate of the entering CO group from a comparison of the CO stretching frequencies observed with those expected for $HRe(CO)_5$ and $Re_2(CO)_{10}$. The spectra of the enriched $Re_2(CO)_{10}$ indicated that substitution was in the radial position, and the mechanism shown in Figure 1 was proposed to account for this. The enhanced bands were of the mono-^{13}CO radially substituted complex and provide additional data for force constant calculations. However, such calculations have not as yet been reported.

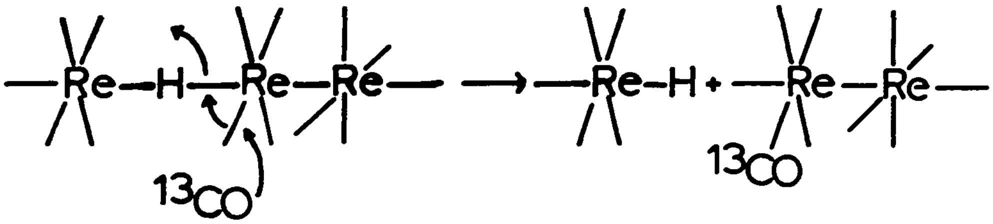

Figure 1.-Mechanism for the reaction of $HRe_3(CO)_{14}$ with CO.

Bor[14] has recently reported the preparation of ^{13}CO-enriched $Mn_2(CO)_{10}$ by irradiating a *n*-hexane solution of $Mn_2(CO)_{10}$ in contact with ^{13}CO-rich (22.5%) carbon monoxide for several hours. It was thus confirmed that the four weak bands resulted from one of the two $Mn_2(^{12}CO)_9$-(^{13}CO) isomers as assigned earlier by Parker and Stiddard.[15] Moreover, a fifth mono-^{13}CO band was observed, as well as other very weak bands which were shown to belong to di-^{13}CO substituted molecules. Using the ^{13}CO bands observed, along with the previously assigned infrared active CO fundamentals,[15] $(2\underline{b}_2 + \underline{e}_1)$, a set of force constants were calculated. These were then used to back-calculate the infrared forbidden frequencies $(2\underline{a}_2 + \underline{e}_2 + \underline{e}_3)$.

ii. Halopentacarbonylmetal Complexes

a. Mechanism of CO exchange

The mechanism of CO exchange in halopentacarbonylmetals and the relative reactivities of the five CO's have stimulated an interesting discussion.[16] One of the CO groups in such octahedral complexes is in a position *trans* to the halogen and is therefore different from the other four equivalent CO's which are *cis* to the halogen.

Early carbon monoxide exchange studies on $Mn(CO)_5X$ (X = Cl, Br, I) were carried out by Wojcicki and Basolo,[17] and by Hieber and Wollman[12] using ^{14}CO. The former research group suggested that in toluene at 30°, the four equatorial carbonyl groups exchanged at a much faster rate than did the axial group; while the latter group, who conducted a similar series of experiments in benzene at 40°, came to the same conclusion for the chloride and bromide but found that all five carbonyl groups exchanged at approximately the same rate in the iodide. These results were explained as follows: In d^6 octahedral systems, the d_{xy}, d_{xz} and d_{yz} pairs of electrons back-donate *via* π-bonding into empty p orbitals on the carbonyl carbon atoms. The geometry of these orbitals entail that ligands *trans* to one another compete for the same sets of d orbitals. Thus, the CO *trans* to X (a poor π-bonder) is in competition with X and as a result is more π-bonded than it would be if in competition with CO for the d orbitals, as is the situation for the equatorial carbonyl groups.

The results of the radiocarbon monoxide studies have, however, recently been called to question. Investigations by Kaesz *et al.*[18] and by Johnson *et al.*[19,20] who used infrared techniques to study the exchange reactions of the $Mn(CO)_5X$ compounds with ^{13}CO and $C^{18}O$, respectively, indicated that there was little or no difference in the specific rates of substitution at the two non-equivalent positions. Johnson *et al.*[20] suggested that this discrepancy could be explained by a mechanism in which it is assumed that even though the loss of CO occurs preferentially from the equatorial position, there exists a rapid equilibration of CO groups such that the axial and the three equatorial CO groups in the five-coordinate intermediate $Mn(CO)_4X$, are apparently equivalent.

This proposal has, however, been shown to be incorrect by Brown,[21] who invoked the principle of microscopic reversibility to support his argument. This principle dictates that if the CO is lost preferentially from the equatorial position, then no matter what modes of equilibration prevail in the five-coordinate intermediate, addition of the labelled CO will inevitably occur in the equatorial position with the same extent of preference which marked the loss of the original CO. Brown prefers to explain the apparent equality of the exchange rates in the axial and equatorial positions in $Mn(CO)_5X$, [as well as in $Mn(CO)_5H$[22,23] and $Re(CO)_5H$[23]] by proposing that these results are not related to the kinetics of the substitution but are due instead to a non-dissociative exchange of axial and equatorial CO groups which is fast relative to the dissociative exchange. Easy pathways for such an intramolecular axial-equatorial interchange in $Mn(CO)_5X$ may take place either *via* a twisting motion (Figure 2), or by the migration of X to an adjacent carbon atom.[21] It is significant to remember that $Re_2(CO)_{10}$ retained its radially substituted ^{13}CO in that position,[13] and also that in the case of $Cr(CO)_4$(*o*-phen), where a ligand migration is not possible, different rates were actually observed[9] for the two sets of different CO's.

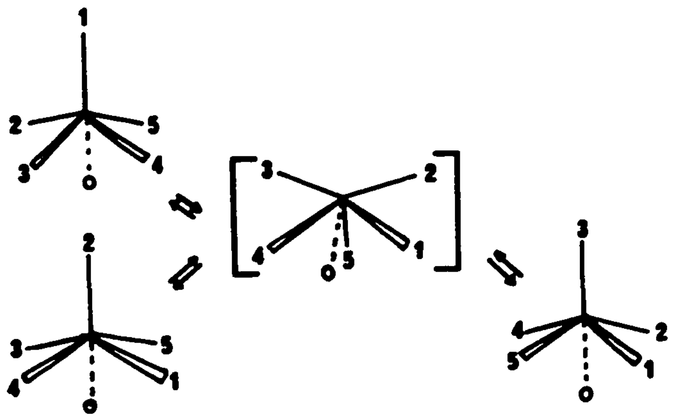

Figure 2.-Possible pathways for intramolecular rearrangement in $Mn(CO)_5X$ complexes.

Cetini *et al.*[24] have studied the isotopic exchange reactions of $Re(CO)_5X$ (X = Cl, Br, I) under kinetic conditions in toluene, using

^{14}CO. They found that in agreement with the i.r. data of Kaesz *et al.*,[18] the five carbonyls were kinetically equivalent. Provided that the concentration of CO was not less than 8-10mM, the reactions were found to follow a first-order rate law which was independent of CO concentration, suggesting that a dissociative mechanism was involved, with the rupture of an Re-C bond being the slow rate-determining step. However, with CO concentrations of the order of 1mM, the observed rate constants were found (1) to be higher than those encountered when the CO concentration was 8-10mM, (2) to decrease with decreasing complex concentration, and (3) to increase with decreases in CO concentration. These interesting observations were explained by assuming that at low CO concentrations, a small amount of dimer $[Re(CO)_4X]_2$ is formed whose exchange rate is faster than that of $Re(CO)_5X$. The concentration of dimer decreases with a decrease in monomer concentration and increases with a decrease in the CO concentration, according to the equilibrium

$$2Re(CO)_5X \rightleftarrows [Re(CO)_4X]_2 + 2CO$$

b. Assignments and force constant calculations

As already mentioned, Kaesz *et al.*[18] have studied the exchange reaction of $Mn(CO)_5Br$ with ^{13}CO. They used their results to assign all of the infrared absorptions in the CO stretching region (including the many minor peaks which had hitherto been neglected) of the $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) complexes to the modes of the all-^{12}CO derivatives (95% natural abundance) and the monoisotopic species $M(^{12}CO)_4(^{13}CO)X$ (4% ^{13}CO in the radial, and 1% ^{13}CO in the axial position). They accepted the previous assignments which had been given for the $\underline{a}_1$ (radial), $\underline{e}$, and $\underline{a}_1$ (axial) vibrations and, utilizing this as a base, made use of the intensities and the relative positionings of the minor peaks which had been found to increase on enrichment, to provide an assignment for the monoisotopically substituted species. Six of the assigned frequencies were then used to calculate uniquely the force constants in the CO block. (For the $M(CO)_5X$ system, once the constraint of energy factoring is placed on the force field, five force constants are sufficient to describe the high energy CO block. These are shown diagramatically in Figure 3.) The force constant calculations served as a confirmation of the assignments since very close agreement (± $0.1cm^{-1}$) between observed and calculated frequencies was obtained.

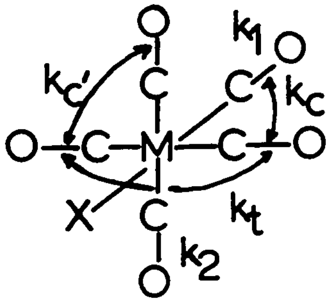

Figure 3.-Idealized structure and Cotton-Kraihanzel parameters for $M(CO)_5X$.

The calculation of the two remaining frequencies which had not been used as input and which were predicted to within $3cm^{-1}$ also served as an independent check on the validity of the assignment. An interesting outcome of these calculations was the distribution of the $\underline{a}_1$ (radial) absorption. The results indicated increased contributions of axial motion in the order Cl<Br<I. The increased contributions parallel the observed absolute intensities of the high energy $\underline{a}_1$ mode.

Johnson *et al.*[20] studied the exchange of $C^{18}O$ with the CO groups of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ by following the variation of the infrared spectra in the CO stretching region with time. They assigned the fundamental modes in the spectrum of the parent molecule in a very interesting manner which made no empirical assumptions apart from the one that CO stretching frequencies depend, to a good approximation, on a force constant function and on the reduced masses of isolated molecules. Under these conditions isotopic substitution in a molecule would produce a maximum effect calculated by multiplying the frequencies by the square root of the ratio of the initial and final reduced masses. When substituting $C^{18}O$ for $C^{16}O$ a decrease in frequency of about $48cm^{-1}$ would be expected for a frequency of $2000cm^{-1}$. Johnson *et al.* pointed out that if only partial substitution occurred, the frequency shifts would be close to the maximum expected for those vibrations involving mainly the substituted groups, close to zero for those vibrations associated only with unsubstituted groups, and of intermediate values for those vibrations involving both types of CO groups. Furthermore, if a specific vibration involved n carbonyl groups, then each stage in the partial substitution would provide a set of frequencies for a total of (n-1) closely grouped sets. The number of frequencies in each set would be equal to the number of isomers possible. Thus, for $Mn(CO)_5Br$, since only one band was observed below $2000cm^{-1}$ (at $1958cm^{-1}$) it became immediately clear that this band could only be the $\underline{a}_1$ axial mode. Furthermore, there was only one band between the strong band at $2052cm^{-1}$ and its maximum possible shift at $2000cm^{-1}$.

This automatically branded this vibration as the e mode. Between 2135 and 2087cm^{-1}, three intermediate sets were detected (with partial splittings of the sets into components) indicating that the vibration at 2135cm^{-1} was associated with at least four groups, and therefore had to be assigned to the a_1 radial mode. The only other bands which appeared on substitution were around 2070cm^{-1} and were associated with the i.r. inactive b_1 mode, which had therefore to lie above this frequency.

The force constants for the CO block of $Mn(CO)_5Br$ were also calculated by Johnson *et al.*[20] who adjusted the constants until computation resulted in a good agreement between observed and calculated frequencies for all those bands in the spectra which were not influenced by overlap, and thus uniquely assignable.

iii. Miscellaneous Substituted Metal Carbonyl Complexes

Subsequent to the work of Kaesz *et al.*[18] on the halopentacarbonyls, Braterman, Harrill, and Kaesz[23] studied the spectra of isotopically substituted $HMn(CO)_5$, $DMn(CO)_5$, $HRe(CO)_5$, and $DRe(CO)_5$. They assigned all the observed maxima with the aid of force constant calculations, and ^{13}CO enrichment, to the carbonyl stretching modes of the all-^{12}CO species, and of the principal isotopic species present in natural abundance. A number of interesting observations were made. Firstly, the spectrum of $DRe(CO)_5$ showed, not only the expected shift in the ReH stretching frequency, but also distinct shifts in at least two of the carbonyl absorptions, automatically labelling them as a_1 modes. These are the ^{12}CO and ^{13}CO modes associated with the axial CO group *trans* to H. No perceptible shift was observed in the band assigned to the a_1 radial mode, indicating less mixing of this mode with the rhenium-hydrogen stretching vibration. This was claimed to be authenticated by the calculation of *cis* and *trans* interaction constants between the ReH and CO stretching vibrations, since the former was found to be close to zero. The second point was that inclusion of the ReH stretching frequency (∿ $1800\mathrm{cm}^{-1}$) in the force constant calculations of the CO block, provided for only small changes in the calculated values. This gave some added confidence in the procedure of high-energy factoring, since the next closest frequencies were in the $600\mathrm{cm}^{-1}$ region. Thirdly, the five CO groups were found to exchange at qualitatively the same rate, in agreement with prior studies on $HMn(CO)_5$ using radiocarbon monoxide.[22]

Noack and Calderazzo[25] have carried out an elegant series of experiments to choose between the carbonyl insertion (A) and the metal migration (B) mechanisms proposed for the carbonylation of $CH_3Mn(CO)_5$ (Figure 4). Since their report provides an excellent example of the power of isotopic studies in the determination of reaction mechanisms it will be reviewed in some detail.

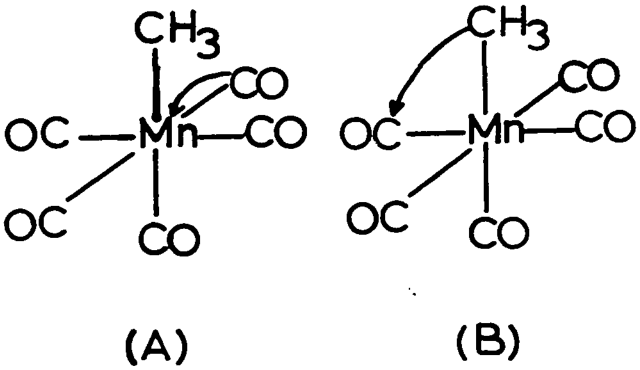

Figure 4.-Mechanisms for the carbonylation of $CH_3Mn(CO)_5$; (A) carbonyl insertion (B) methyl migration.

1. The initial carbonylation of $CH_3Mn(CO)_5$ with 50%- enriched ^{13}CO indicated that the latter was present only in the position *cis* to the acetyl group in the resulting acetyl manganese carbonyl complex. This indicated that the incoming ^{13}CO was not directly inserted from the gas phase into the $Mn-CH_3$ bond, thus providing definite proof for either scheme (A) or (B), though no decision between them. The spectra of the product further indicated that no significant isomerization occurred, since this would have led to a statistical distribution of the ^{13}CO.

2. Decarbonylation of $CH_3{}^{13}COMn(CO)_5$ [prepared from $CH_3{}^{13}COCl$ and $NaMn(CO)_5$] gave exclusively *cis*-$CH_3Mn(CO)_4{}^{13}CO$, indicating that both carbonylation and decarbonylation occur by the same mechanism in accord with the principle of microscopic reversibility.

3. Decarbonylation of *cis*-$CH_3COMn(CO)_4{}^{13}CO$ obtained in (1) yielded a 2:1 ratio of *cis* and *trans*-$CH_3Mn(CO)_4{}^{13}CO$ as evident from the intensities of radial and axial ^{13}CO modes. Since, by carbonyl insertion no *trans* product would be expected, this result pointed to a methyl migration mechanism.

4. Carbonylation of *cis*-$CH_3Mn(CO)_4{}^{13}CO$ with normal CO gave acetylmanganese pentacarbonyl which contained the *cis*, the *trans*, and the $^{13}COCH_3$ products in a 2:1:1 ratio totally consistent with methyl migration, and completely contrary to the 0:1:3 ratio expected for carbonyl insertion.

5. The final recarbonylation with normal CO of the 2:1 mixture of *cis*-: *trans*-$CH_3Mn(CO)_4{}^{13}CO$ as obtained in (3), furnished a 4:1:1 ratio of *cis*-and *trans*-$CH_3COMn(CO)_4{}^{13}CO$, and $CH_3{}^{13}COMn(CO)_5$, respectively, again only in agreement with the methyl migration mechanism.

From the above experiments it was concluded that $CH_3Mn(CO)_5$ is converted to $CH_3COMn(CO)_5$ by CO *via* a mechanism whereby a methyl group is directly displaced by the incoming nucleophile followed by, or concurrent with, a methyl migration to an adjacent carbon monoxide group. Noack, Ruch,and Calderazzo[26] have used ^{13}CO labelling in a similar manner to help elucidate the mechanisms of the reactions of $CH_3Mn(CO)_5$ and $CH_3COMn(CO)_5$ with PPh_3.

In a separate publication Noack[27] detailed the assignment of the CO stretching frequencies of methyl and acetylmanganese pentacarbonyl highly enriched with ^{13}CO in either the *cis* or *trans* position, and in the acetyl group. For the methyl derivatives, the results agree within the limits of experimental error to those of Cotton, Musco, and Yagupsky[28] who used the naturally abundant amount of ^{13}C-compound present to make the assignments and calculate the force constants.

In compounds of the type 9,10-$L_2Mn_2(CO)_8$, the mono-^{13}CO derivative occurs naturally to the extent of 8.15% and the di-^{13}CO derivative to the extent of 0.32%, the disubstituted species spanning four isomers each with a 0.08% abundance. Lewis, Manning, and Miller[29] calculated complete sets of Cotton-Kraihanzel force constants and in order to test their assignments, the frequencies of some ^{13}CO containing molecules were computed and found to compare very well with weak bands observed in the spectra.

Gay and Graham[30] have measured the spectra of mono-^{13}CO substituted $X_3M'Mn(CO)_5$ complexes (X = Ph, Br; M' = Ge, Sn) in order to compare the calculated values of the axial and radial CO stretching force constants. It had earlier been proposed, and later substantiated by numerous calculations, that the radial force constant (k_2) was higher than the axial one (k_1), but Gay and Graham found that for $Ph_3GeMn(CO)_5$ and its tin analogue, k_2 was less than k_1. They explained this as a breakdown of one of the premises for making the $k_1 < k_2$ generalization, namely, that the incoming ligand is a weaker π-acceptor than CO.

C. GROUP VIII

i. Binary Metal Carbonyl Complexes

a. Iron pentacarbonyl

Keeley and Johnson[10] reported in 1959, that $Fe(CO)_5$ was inert towards exchange with radioactive ^{14}CO under uncatalyzed conditions, but underwent exchange slowly in the presence of light. Later, Basolo, Brault, and Poë[22] found that the exchange of $Fe(CO)_5$ and $Fe(CO)_4PPh_3$ with ^{14}CO was catalysed by the presence of trifluoroacetic acid in 1,2-dichloroethane.

Infrared studies on the $Fe(CO)_5$ exchange were first carried out by Bor[31] who increased the ^{13}CO content of $Fe(CO)_5$ by exposure of an *n*-heptane solution in an atmosphere of ^{13}CO to sunlight for one hour. Four new bands were observed and assigned to the two mono-^{13}CO molecules. Based on these data, force constants were calculated, as were the infrared frequencies of the all-^{12}CO and variously substituted species. The calculations yielded the values 2113.8 and 2031cm^{-1} for the two infrared inactive $\underline{a}'_1$ frequencies of $Fe(^{12}CO)_5$, in excellent agreement with the Raman values at 2114 and 2031cm^{-1} reported by Stammreich, Sala, and Tavares.[32] The agreement with the calculated values of Haas and Sheline,[33] who used naturally abundant ^{13}CO frequencies in their calculations, is less good.

A study of the mechanism of CO exchange with $Fe(CO)_5$ and $Fe(CO)_4PPh_3$ under various conditions has been reported by Noack and Ruch.[34] A mixture of normal $Fe(CO)_5$ and $Fe(C^{18}O)_5$ did not show any scrambling of the CO groups, even under the effect of the Nernst glower in the infrared spectrophotometer, although rapid exchange and complete scrambling occurred in the presence of supported palladium. The latter was also found to promote rapid exchange, and a statistical distribution, of ^{13}CO or $C^{18}O$ with $Fe(CO)_5$. Even at low temperatures (-20°), no preferential exchange was observed at the axial or equatorial positions. The same results were also obtained in light-induced reactions.

Basolo, Brault, and Poë[22] found that the axial and equatorial CO groups in $Fe(CO)_5$ exchanged at different rates in the presence of trifluoroacetic acid, while $Fe(CO)_4PPh_3$ only exchanged three CO groups. These conclusions were recently contradicted by the results of Noack and Ruch.[34] For both complexes, the latter group found that the products were distributed in a pattern which was far from equilibrium and with the monosubstituted species being highly disfavoured with respect to the higher substitution derivatives. Furthermore, no preference for axial or equatorial substitution was observed, and when the solution was equilibrated by using ultraviolet illumination, the pattern of the spectrum was found to change completely with the bands of the mono- and disubstituted species increasing at the expense of the higher substitution products. These surprising results led to the conclusion that in the CF_3COOH catalyzed reactions the simultaneous exchange of two carbonyl groups occurred; this fact could not, however, be explained.

b. Nickel tetracarbonyl

Isotopic substitution on $Ni(CO)_4$ has been carried out both with the aim of calculating force constants, as well as, gathering kinetic data for the elucidation of the exchange mechanism.

Until recently, there existed a great deal of confusion as to the exact exchange mechanism involved.[16] Early studies by Basolo and

Wojcicki[11] with ^{14}CO indicated that the rate was independent of the ^{14}CO concentration. The same first-order rate law was found for the substitution reaction of $Ni(CO)_4$ with PPh_3 to give $Ni(CO)_3PPh_3$.[35] The confusion arose, however, when temperature dependence studies of this reaction showed that its activation parameters were markedly different from those obtained from the ^{14}CO exchange study.[36] These results suggested that the two first-order processes, exchange and substitution, occurred by different mechanisms.

The solution to the problem came with the work of Day, Basolo, and Pearson[37,38] who reported new measurements of the rates of CO exchange and PPh_3 substitution obtained by using infrared spectrophotometry and $C^{18}O$ for the exchange studies in the gas[38] and liquid phase.[37,38] The results did not confirm those obtained previously for the radiocarbon monoxide exchange studies, and the conclusion was reached that both nucleophiles reacted by the same first-order mechanism, that is, by a rate-determining CO dissociation step followed by a rapid reaction of the active intermediate. This conclusion was substantiated by experiments which showed that the two nucleophiles compete for the same intermediate (presumably $Ni(CO)_3$), which is captured five times faster by the PPh_3 than by the $C^{18}O$. The anomalous results obtained in the exchange studies by the ^{14}CO radioactivity counting technique were explained as being due to an exchange of the volatile $Ni(CO)_4$ in the gas phase which was at room temperature, rather than at the low temperature recorded for the exchange solution.[16,38]

Two further interesting aspects of the $C^{18}O$ exchange study of $Ni(CO)_4$ are worth mentioning. Firstly, the rate data were gathered from the formation and subsequent reaction of $Ni(C^{16}O)_3(C^{18}O)$, since the kinetically simpler study of the decay of $Ni(C^{16}O)_4$ was not possible because of the superimposition of bands. Secondly, it was found that a mixture of $Ni(C^{16}O)_4$ and $Ni(C^{18}O)_4$ in the gas phase underwent a very fast scrambling process at a rate very much greater (> 100 times) than the CO exchange, to give an equilibrium mixture of $Ni(C^{16}O)_n(C^{18}O)_{4-n}$. In *n*-hexane solution, however, the same scrambling occurred at a much slower rate (< 0.01 times) than CO exchange. This was in contrast to the exchange process which occurred at about the same rate in both phases, and suggested the possible formation in the gas phase of a binuclear species with bridging CO groups which then decomposed to the scrambled species.

A number of spectroscopic investigations of $Ni(CO)_4$ with isotopic carbon monoxide have been reported.[38-41] Bor[40] studied samples in *n*-hexane enriched with ^{13}CO to a maximum extent of 22% and assigned all the absorption bands to the different ^{12}CO and ^{13}CO containing molecular species. The infrared- inactive $\underline{a}_1$ frequencies of $Ni(^{12}CO)_4$ and $Ni(^{13}CO)_4$ were determined by extrapolating the $\underline{a}_1$ frequencies obtained for the other molecular species. The CO stretching force constant and the CO-CO interaction constant were computed and then used to calculate the frequencies of mixed ^{13}CO- containing nickel carbonyl molecules; these were found to agree within ±0.4cm^{-1} of the experimentally observed values. Haas and Sheline[33] have also reported the bands of $Ni(^{12}CO)_3(^{13}CO)$ from naturally abundant species and have compared the observed and calculated spectra of $Ni(^{12}CO)_n(^{13}CO)_{4-n}$.

Bouquet and Bigorgne[39] synthesized $Ni(C^{18}O)_4$ by reacting $C^{18}O$ with pulverized Ni at room temperature. They measured the Raman spectrum of the liquid and the infrared spectrum of the gas, and compared the observed frequencies with those of $Ni(C^{16}O)_4$. A number of force constants were calculated and used to compare the observed and calculated frequencies for samples containing a sizable amount of mono- and di-$C^{18}O$ substituted species. Their frequencies are in quite good agreement with those reported later by Day, Basolo, and Pearson.[38]

A very thorough spectroscopic investigation has been carried out by Jones, McDowell, and Goldblatt[41] who reported the infrared spectra of gaseous $Ni(^{13}CO)_4$ and $Ni(C^{18}O)_4$ and the infrared and Raman spectra of CCl_4 solutions of these isotopic molecules. The frequencies of all three complexes ($Ni(^{l}C^{k}O)_4$; l, k = 12,16,13,16,12,18) were meticulously assigned and used for the calculation of general quadratic force constants. An interesting result of this study was that the ^{13}CO and $C^{18}O$ produced markedly different shifts in the low-frequency ν(MC) and δ(MCO) modes. Furthermore, the shifts were observed to be dependent on the phase. For example, the $\underline{a}_1$ ν(NiC) mode was shifted by -3.6 and -10.9cm^{-1} for $Ni(^{13}CO)_4$ and $Ni(C^{18}O)_4$, respectively, in the gas phase, but by -3.4 and -18.8cm^{-1} in CCl_4 solution.

c. Dicobalt octacarbonyl

Although Bor[42] prepared $Co_2(CO)_8$ enriched with 22.5% ^{13}CO, in an equilibrium mixture, he did not report the spectrum, stating that it would be published at a later date. This work has still to be published. It may be mentioned here, however, that $Co_2(CO)_8$ is known to exchange with ^{14}CO at a fast rate,[10,11] and that all eight carbonyl groups are equivalently reactive.[22] The infrared experiments of Noack[43] provided an obvious explanation for this behaviour when it was found that, in solution, $Co_2(CO)_8$ is present as a carbonyl bridged species in rapid equilibrium with a non-bridged one (p.14). In this way, the carbonyl groups can scramble rapidly and show equivalent reactivities.

ii. Substituted Group VIII Metal Carbonyl Complexes

The first report on the spectroscopic investigation of an isotopically substituted metal carbonyl complex appeared in 1961 by McDowell, Horrocks, and Yates[44] who studied the ^{13}CO and ^{15}NO enriched i.r. spectra of cobalt tricarbonyl nitrosyl, $Co(CO)_3NO$, in the vapour phase, and used their results for a normal coordinate treatment. The exchange with ^{13}CO provided proof that a strong band at $2010cm^{-1}$ observed in the parent spectrum was due to a ^{13}CO stretch of the isotopic species $Co(^{12}CO)_2(^{13}CO)NO$. No data were given on the spectra of molecules containing more than one ^{13}CO ligand apart from the mention of an additional band at $2090cm^{-1}$.

Bor[40] later investigated the spectrum of ^{13}CO enriched (22%) $Co(CO)_3NO$ and assigned a band at $2091.2cm^{-1}$ to the in-phase coupling of the two a' symmetry coordinates in $Co(^{12}CO)_2(^{13}CO)NO$. Bor also reported the other modes for the mono- and di-^{13}CO molecules and calculated the CO and NO stretching force constants, and the CO-CO and NO-CO stretch-stretch interaction constants, the latter being assumed to be the smaller of the two.

Haas and Sheline[33] have also reported two frequencies for $Co(^{12}CO)_2(^{13}CO)NO$ and one frequency for $Co(^{12}CO)(^{13}CO)_2NO$ from the spectrum of the naturally abundant complex, but their values are quite different from those of Bor.[40]

The first complete study of a binuclear carbonyl was also carried out by Bor,[42] on $Hg[Co(CO)_4]_2$. He reported that this complex was very stable and exchanged CO very slowly, and that he therefore had to use an indirect method to prepare enriched samples of the complex. This consisted of treating ^{13}CO enriched $Co_2(CO)_8$ with Hg. There was no mention in his paper of the ^{14}CO exchange work with $Hg_2[Co(CO)_4]_2$ which was found by Breitschaft and Basolo[45] to proceed at reasonably fast rates. Bor determined the infrared inactive CO stretching frequencies of $HgCo_2(^{12}CO)_8$ from force constant calculations based on the frequencies of the $HgCo_2(^{12}CO)_7(^{13}CO)$ molecules. He found that the axial CO stretching force constant was higher than the equatorial one, and the CO-CO interaction constants across the metal atoms were all less than 0.07 mdyn/Å. The inactive frequencies calculated were not in very good agreement with prior Raman data, but were found to be more applicable in the assignment of the first CO stretching combination spectrum.

Nagy-Magos,Bor, and Marko[46] studied the insertion reaction of CO into the C-Co bond by using ^{13}CO as the carbonylating agent. It was thus shown that when (triphenylphosphine)benzylcobalt tricarbonyl, $Co(CO)_3(PPh_3)(CH_2Ph)$, was carbonylated to give (triphenylphosphine)(phenylacetyl)cobalt tricarbonyl, $Co(CO)_3(PPh_3)(COCH_2Ph)$, that the acyl group is formed by incorporation of a carbonyl ligand whereas the CO from the gas phase enters the coordination sphere of the cobalt atom as a new ligand.

Exchange studies on *cis*-$Fe(CO)_4I_2$ with $C^{18}O$ have been reported by Johnson *et al.*[47] who followed the variation of the infrared spectrum in the CO stretching region with time. The *cis*-$Fe(CO)_4I_2$ spectrum was assigned and an optimum set of force constants was determined.

The naturally occurring ^{13}CO species for *cis*-$Fe(CO)_4Br_2$ were also used to calculate a set of force constants.

Butadienetricarbonyliron(O), $C_4H_6Fe(CO)_3$, was found by Warren and Clark[48] to undergo photochemical or thermal exchange with ^{13}CO, with very little concomitant replacement of butadiene. The Cotton-Kraihanzel force constants were calculated, and these were then used to calculate all the ^{13}CO frequencies. Isotopic enrichment was used to verify the frequencies of the mono- and di-^{13}CO substituted species. The calculations showed that one CO site was clearly different from the other two. The frequencies from the natural abundance of ^{13}CO in $C_4H_6Fe(CO)_2PF_3$ were used to calculate force constants for this complex. It thus became evident that the PF_3 occupied a unique position, the two remaining CO groups being in equivalent positions.

Johnson *et al.*[49] have studied the exchange of $C^{18}O$ with CO groups of the series of bridged complexes $Rh_2(CO)_4X_2$ (X = Cl, Br, I, SEt, SPh) with time. The CO stretching frequencies for the various isotopically substituted species were calculated and the observed spectra assigned. In their force constant calculations Johnson *et al.* assumed the interaction constant between two CO groups on different metals to be smaller than that between two CO groups on the same Rh atom.

A table has been provided in the Appendix to this part of the thesis which summarizes the isotopic CO exchange studies performed to date.

CHAPTER III VALIDITY AND APPLICABILITY OF APPROXIMATE CO STRETCHING FORCE FIELDS

In 1962, Cotton and Kraihanzel[50] proposed a simple model for analyzing and assigning the infrared active carbonyl stretching vibrations of octahedral complexes. The model involved qualitative and semiquantitative inferences from valence theory concerning the signs and relative magnitudes of CO stretching force constants and the various interaction constants between the CO groups. Their conclusions were the following:

1. All the CO-CO stretching interaction constants should have positive values.
2. The value of the interaction constants between pairs of *cis* and *trans* CO groups should be expected to be in approximately a 1:2 ratio.
3. Substitution of the CO groups by ligands which make less demand for the metal $d\pi$ electrons should cause a steady decrease in the remaining CO stretching force constants.
4. CO groups in positions *cis* to substituents with the above characteristic, should have higher stretching force constants than those *trans* to such substituents.
5. The CO-CO stretching interaction constants should increase with increasing substitution of CO by ligands of lower π-bonding ability.

Furthermore, a high-frequency separation was assumed, as was the impossibility of detecting any meaningful difference between various *cis* interaction constants which were therefore set equal.

Since then this model has been applied to an exceedingly large number of carbonyl complexes. In fact, all the force constant calculations performed in the studies described in Chapter II with the exception of those by Bouquet and Bigorgne,[39] by Jones, McDowell, and Goldblatt,[8,48] and by McDowell, Horrocks, and Yates,[44] utilized modified versions of what has come to be called the Cotton-Kraihanzel (C-K) force field. The C-K force field has been criticized as to its physical correctness and it would therefore seem worthwhile to examine these critiques in an attempt to assess the merits or demerits of its approach.

The most persistent critic of the C-K force field has been Jones[8,41,51,52] who has time and again compared values of the primary CO stretching force constants as well as the CO-CO interaction constants calculated using both the C-K and more rigorous force fields. In an initial correspondence, Jones[51] pointed out that the "approximate" calculations could be very deceiving as to the absolute and relative magnitudes of the CO-CO interaction constants. Furthermore, rigorous calculations using anharmonic as opposed to harmonic frequencies were found to be misleading. He did concede, however, that the "approximate" CO stretching constants were in the vicinity of the rigorously calculated ones and that trends among similar compounds (e.g. $M(CO)_5L$ and $M(CO)_5L'$) would therefore be meaningful.

In a subsequent correspondence, Jones[52] once again reported the effects of the inclusion of anharmonicity corrections and the use of a generalized force field on the CO stretching and CO-CO interaction constants. His italicized conclusion was that

> *"the CO-CO interactions calculated with a CO-factored force field have no fundamental significance, either in their relative or absolute values."*

Nevertheless, he does mention that the effects on the CO force constants due to the utilization of a general force field cancel one another, and the errors that arise result mainly from a neglect of the anharmonicity terms. Jones concluded that it may be possible to evaluate relative CO bond strengths by comparing CO stretching force constants for different carbonyls using the non-rigorous method assuming an uncertainty of ±0.1 mdyn/Å in the relative values.

In a reply to Jones'[52] correspondence, Cotton[53] fails to see that Jones' "computations prove anything of practical importance about the Cotton-Kraihanzel (C-K) force field." Cotton further states that he himself has repeatedly stressed the word "relative" when describing the merits of the calculated force constant values, and continues with,

> "Any further demonstration that neglect of anharmonicity, solvent effects, incomplete force fields, etc., introduces error into the absolute values of the CO force constants is simply flogging an already well-lacerated dead horse."

Bower and Stiddard[54] also respectfully suggest that although the C-K model is sometimes useful as a framework within which to discuss the observed frequencies, extreme caution should be exercised in the interpretation of the quantitative significance of the calculated force constants even in structurally related molecules. They also propose[54,55] that, frequently, the calculation of C-K force constants does nothing but transform data from one form to another, and that the frequencies themselves can be used for qualitative descriptions, etc.

Loutellier and Bigorgne[56] have shown that when calculating CO stretching force constants of metal carbonyl derivatives, the adjacent M-C bonds must, at least, be taken into account. If not, the calculations may in certain cases indicate variations in the CO force constant opposite to the real variations. Thus, in the series $Ni(CO)_{4-n}(PF_3)_n$ $(n = 0 - 3)$ the CO force constants were found to increase with increased substitution when the C-K force field was used, and decrease when a more rigorous calculation was performed.

Notwithstanding these criticisms one very important advantage of the factored-off CO stretching model (which is closely related to the Cotton-Kraihanzel force field without using the approximations in the interaction constants) has been emphasized by Bor.[31] This is that the spectra of isotopically substituted carbonyl molecules (^{13}CO or $C^{18}O$) can be calculated with a high degree of accuracy. Ample illustration of this advantage has been given in Chapter II.

CHAPTER IV SPECTROSCOPIC STUDIES OF ^{13}CO-ENRICHED *cis*-$Fe(CO)_4Br_2$ AND *cis*-$Fe(CO)_4I_2$

A. INTRODUCTION

The infrared spectra of the *cis*-$Fe(CO)_4X_2$ molecules (X = Cl,Br, or I) in the CO stretching region have been the subject of numerous investigations over the past few years.[47,57-62] In most of these, the chief point of interest has been the assignment of the fundamentals of the all-^{12}CO molecules. The weak absorptions in the spectra have been either neglected or attributed without actual proof[47,58] to the absorptions of ^{13}CO substituted molecules present in natural abundance. While the present work was in progress, Johnson *et al.*[47] reported spectroscopic data for the exchange reaction of *cis*-$Fe(CO)_4I_2$ with $C^{18}O$. The CO stretching frequencies observed during the exchange were assigned to the all-^{12}CO molecule and a number of $C^{18}O$ substituted species. Johnson *et al.* also studied the spectrum of unenriched *cis*-$Fe(CO)_4Br_2$ and without any direct proof assigned the minor peaks observed to the absorptions of specific, naturally occurring ^{13}CO substituted molecules. The proposed assignments for both molecules were supported by calculations of the five force constants in the energy factored CO stretching block of the (FG^{-1}) matrix.

In this section of the thesis the complete assignment of the CO stretching modes of the principal species occurring in natural abundance in *cis*-$Fe(CO)_4X_2$(X = Br or I), all-^{12}CO(96%), mono-^{13}CO substitution *cis* to X(2%), and mono-^{13}CO substitution *trans* to X(2%) will be given.*

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* The results of this study have been published, see ref.63

The ^{13}CO modes have been experimentally verified through exchange with 50% ^{13}C-enriched CO. The CO groups *cis* and *trans* to I in *cis*-$Fe(CO)_4I_2$ are observed to be approximately equally enhanced during exchange in agreement with previous radiocarbon monoxide studies.[17,64]

B. EXPERIMENTAL

The *cis*-$Fe(CO)_4X_2$ compounds were prepared according to the methods described in the literature by Hieber and Bader.[65]

i. ^{13}C-Enriched *cis*-$Fe(CO)_4X_2$

^{13}C-enriched *cis*-$Fe(CO)_4Br_2$ and *cis*-$Fe(CO)_4I_2$ were prepared by exchange at room temperature in cyclohexane with 50% ^{13}C-enriched carbon monoxide. For this purpose the exchange apparatus shown in Figure 5 was designed, and the following procedure used. A solution of the appropriate carbonyl complex was syringed into vessel A, which had a volume of approximately 5ml, after which the rubber septum G was positioned to effectively isolate the system. The solution in A was then cooled by liquid N_2, stopcocks D and E opened, and the system evacuated on a conventional vacuum line. (If the carbon monoxide bulb B was still sealed, stopcock F was also opened and after evacuation of the volume between it and the break-seal, the former was closed and the latter was carefully broken by a glass-enclosed magnet.) The solution was then allowed to warm up to room temperature and the process repeated three or four times to ensure that the solution was completely degassed. After this had been accomplished, stopcock F was opened and the isotopic gas in bulb B was allowed to expand into the vessel A. Stopcock F was then closed and the exchange allowed to proceed. Samples of the solution were withdrawn at appropriate intervals with the syringe C, and their infrared spectra recorded.

Since solutions of the iron compounds were known to decompose and isomerize to the *trans*-complexes[62,71] in the presence of light, the

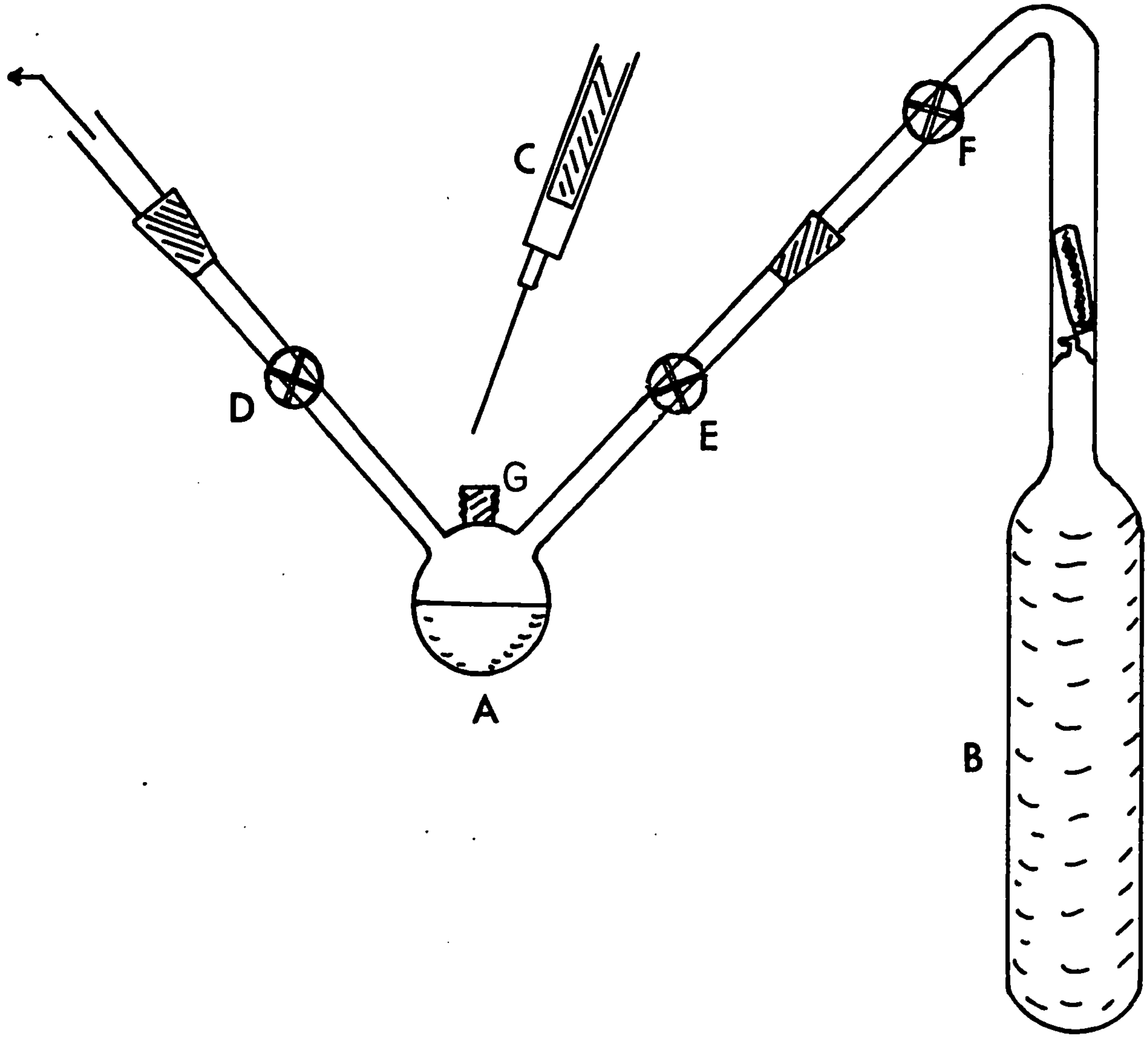

Figure 5.-Reaction vessel for isotopic CO exchange.

reaction vessel A was painted black and the infrared spectra of the samples taken from the reaction mixtures were recorded immediately after their withdrawal. In spite of these precautions, some decomposition of the dibromide still occurred. Fortunately, the decomposition was slow enough to allow identification of the CO stretching frequencies of the various ^{13}CO substituted species present. As expected there was no spectral evidence for the formation of the *trans*-$Fe(CO)_4X_2$ compounds, since the exchange reactions were always carried out in the dark.

ii. Infrared Spectra

The infrared spectra in the CO stretching region were recorded in cyclohexane on a modified Perkin Elmer model 337 grating spectrophotometer equipped with a Texas Instruments Servo/Riter model II expanded-scale recorder. A new pair of matched 1.00mm KBr cells were used for all spectra. The frequencies presented in Table I are the mean values obtained from the spectra of about 10 samples taken from the reaction mixtures throughout the exchanges. The spectra were calibrated against the 2143.2cm^{-1} band of CO and the 1601.4 and 1583.1cm^{-1} bands of polystyrene. The measurement of peak differences for several spectra gave a reproducibility of about ±0.5cm^{-1}, while the absolute accuracy of the frequencies is 1-2cm^{-1}.

iii. Calculations

The idealized geometry and definition of force constants in *cis*-$Fe(CO)_4X_2$ molecules are shown in Figure 6.

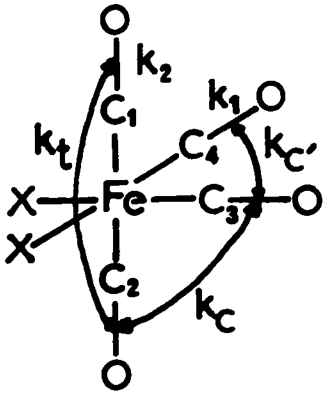

Figure 6.-Idealized structure and Cotton-Kraihanzel parameters for *cis*-$Fe(CO)_4X_2$.

The secular equations relating the force constants and the observed CO stretching frequencies have been reported previously^{50} and are given by

$$\underline{a}_1 \text{ modes : } \quad \begin{vmatrix} \mu(k_2 + k_t) - \lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_1 + k_{c'}) - \lambda \end{vmatrix} = 0$$

$$\underline{b}_1 \text{ mode : } \quad \lambda = \mu(k_2 - k_t) \qquad \underline{b}_2 \text{ mode : } \quad \lambda = \mu(k_1 - k_{c'})$$

The force constants were calculated using an iterative computer program supplied by Dr. J.M. Smith (California Institute of Technology, Pasadena, California) which was modified for use on the IBM 360/75 computer of the McGill University Computing Centre. The computer program was originally written by J.H. Schachtschneider and R.G. Snyder and adjusts the force constants to give a weighted least squares fit of the calculated frequencies to the observed frequencies. The theory and method behind the calculation given by Schachtschneider are described below.

a. Setting up the secular equation

If R is a set of internal valence coordinates which describes the vibrational problem, then the potential energy, V, and the kinetic energy, T, of the vibrating molecules may be written as

$$2V = R^T F R \qquad (1)$$

$$2T = \dot{R}^T G^{-1} \dot{R} \qquad (2)$$

where F is the force constant matrix, G^{-1} is the inverse kinetic energy matrix, and $\dot{R}$ is the time derivative of R.

One requires the transformation matrix L which is defined by

$$R = LQ \text{ or } Q = L^{-1}R \qquad (3)$$

in such a way that the potential and kinetic energy matrices are diagonalized

$$2V = R^T F R = Q^T L^T F L Q = Q^T \Lambda Q \qquad (4)$$

$$2T = \dot{R}^T G^{-1} \dot{R} = \dot{Q}^T L^T G^{-1} L \dot{Q} = \dot{Q}^T E \dot{Q} \qquad (5)$$

where E is the unit matrix and Λ is a diagonal matrix whose elements are related to the vibrational frequencies, $\omega_i(\text{cm}^{-1})$ by

$$\Lambda_{ii} = \lambda_i = 4\pi^2 c^2 \omega_i^2 / N \qquad (6)$$

From (4) and (5) one obtains a commonly used form of the secular equation

$$GFL = L\Lambda \qquad (7)$$

If symmetry coordinates are used, these are related to the internal coordinates by means of an orthogonal matrix U, thus

$$S = UR \qquad (8)$$

and

$$R = U^T S \qquad (9)$$

Substituting (9) into (3) gives

$$S = ULQ = \mathcal{L}Q \tag{10}$$

New symmetrized matrices are defined as follows

$$G' = UGU^T \tag{11}$$

and
$$F' = UFU^T \tag{12}$$

providing the secular equation

$$G'F'\mathcal{L} = \mathcal{L}\Lambda \tag{13}$$

b. Solution of the Secular Equation

The secular equation is solved by using a modification of Jacobi's method for real symmetric matrices. Although GF itself is not symmetric the solution may be accomplished by solving two symmetric problems.

The GF problem is thus solved in two stages. The first stage is the solution of

$$GD = D\Gamma \tag{14}$$

where D is the eigenvector matrix of G and Γ is the diagonal eigenvalue matrix of G. D is orthogonal and the roots are real and positive since G is real and symmetric. Therefore

$$G = D\Gamma D^T \tag{15}$$

Letting W be a matrix defined by

$$W = \Gamma^{1/2}D \tag{16}$$

then
$$G = WW^T \tag{17}$$

For the second stage,the solution of the secular equation of the real symmetric matrix H is considered, where H is defined by

$$H = W^T FW \tag{18}$$

The secular equation may be written as

$$HC = C\Lambda \tag{19}$$

where C is the orthogonal eigenvector matrix of H and Λ is the diagonal eigenvalue matrix of H. Combining (18) and (19) gives

$$W^TFWC = C\Lambda \tag{20}$$

and multiplying this on the left by W

$$WW^TFWC = WC\Lambda \tag{21}$$

whence

$$GFWC = WC\Lambda \tag{22}$$

Since the solution of (7) is desired, it can be seen on comparison with (22) that

$$L = WC \tag{23}$$

L being properly normalized since

$$\begin{aligned}(L^{-1})G(L^{-1})^T &= (C^TW^{-1})G(C^TW^T)^{-1} = C^TW^{-1}WW^T(W^T)^{-1}C \\ &= E\end{aligned} \tag{24}$$

and

$$L^TFL = (C^TW^T)F(WC) = C^THC = \Lambda \tag{25}$$

c. Perturbation of the F matrix

If F_o is an initial trial F matrix, then from (7)

$$GF_oL_o = L_o\Lambda_o \tag{26}$$

and from this the eigenvalues and eigenvectors can be obtained. It is now desired to refine F_o by the amount ΔF such that the solution of

$$\left| G(F_o + \Delta F) - \lambda E \right| = 0 \tag{27}$$

provides the observed frequency parameters. It is assumed that the frequency parameters λ_i are functions of the force constants and that

$$\Delta\Lambda = \Lambda_{obsd} - \Lambda_{calc} \tag{28}$$

may be expanded in terms of the force constants. Keeping only the linear terms this may be written as

$$\vec{\Delta\lambda} = J\vec{\Delta F} \tag{29}$$

where $\vec{\Delta\lambda}$ is a column of $\lambda_{obsd} - \lambda_{calc}$, $\vec{\Delta F}$ is a column of the corrections to the F matrix, and J is the matrix of the force constant Jacobian. It has been shown that

$$\Delta\lambda_i = \Sigma_{k,m} (L_o)_{ik} (L_o)_{mk} \Delta F_{mk} \tag{30}$$

and that the "best" correction to F_o may be found by solving the least squares equation

$$J^T P \vec{\Delta\lambda} = J^T PJ \vec{\Delta F} \tag{31}$$

where P is a diagonal weighting matrix giving the confidence in each observed frequency. Since in most problems it is necessary to assume some relationship between the k(k+1)/2 elements in the F matrix and a smaller set of potential constants Φ, this may be written as

$$\vec{F} = Z\vec{\Phi} \tag{32}$$

where Φ is a column of independent force constants

Thus $$\vec{\Delta\lambda} = JZ\vec{\Delta\Phi} \tag{33}$$

and the least squares equation becomes

$$(JZ)^T P\vec{\Delta\lambda} = (JZ)^T P(JZ)\vec{\Delta\Phi} \tag{34}$$

If a singularity has not been inserted, a solution to (34) is assured, and once $\vec{\Delta\Phi}$ is determined $\vec{\Delta F}$ is computed by

$$\vec{\Delta F} = Z\vec{\Delta\Phi} \tag{35}$$

The equation $$G(F + \Delta F)L = L\Lambda \tag{36}$$

can now be solved and if the calculated Λ is still not satisfactory the process can be repeated until the observed frequency parameters are converged on. The program has a number of built-in checks on the convergence or divergence of the computation which will not be detailed here.

d. Potential energy distribution

The Z matrix introduced in (32) above may be used to calculate the potential energy distribution for each vibration among the elements of Φ. This potential energy distribution is defined as

$$PE = \Lambda^{-1} J Z \Phi \tag{37}$$

where Φ is a diagonal matrix of the elements of the column $\vec{\Phi}$.

C. RESULTS AND DISCUSSION

i. Assignment of the CO Stretching Frequencies Observed During the ^{13}CO Exchange Reactions of *cis*-$Fe(CO)_4I_2$ and *cis*-$Fe(CO)_4Br_2$

The *cis*-$Fe(CO)_4X_2$ molecules possess C_{2v} symmetry for which four infrared active CO stretching vibrations are expected ($\underline{a}_1^{(2)}$, $\underline{a}_1^{(1)}$, $\underline{b}_1$, and $\underline{b}_2$). The symmetry coordinates for these vibrations in terms of internal bond stretching coordinates have been given many times before (*e.g.* see ref.47), and are shown schematically in Figure 7.

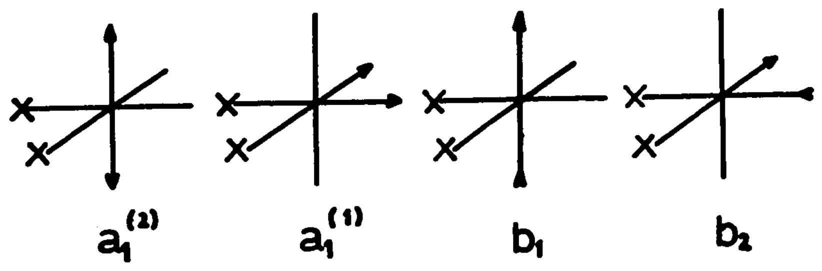

Figure 7.-Symmetry coordinates of *cis*-$Fe(CO)_4X_2$.

The CO stretching absorptions of *cis*-$Fe(CO)_4I_2$ in cyclohexane before and after exchange (3hr) with 50% ^{13}C-enriched CO are shown in Figures 8 and 9, respectively. The actual frequencies and the proposed vibrational assignments are given in Table I.

Noack[58] observed a weak band in the spectrum at 2047cm^{-1} which Johnson *et al.*[47] recently attributed to monosubstitution by naturally occurring ^{13}CO. This is band g in Figure 8 and 9. It is evident that Johnson *et al.* were correct in their assignment of the band as a ^{13}CO mode as it is greatly enhanced during the exchange with ^{13}CO. Similarly, bands b and j are in fact all due to mono-^{13}CO substituted molecules.

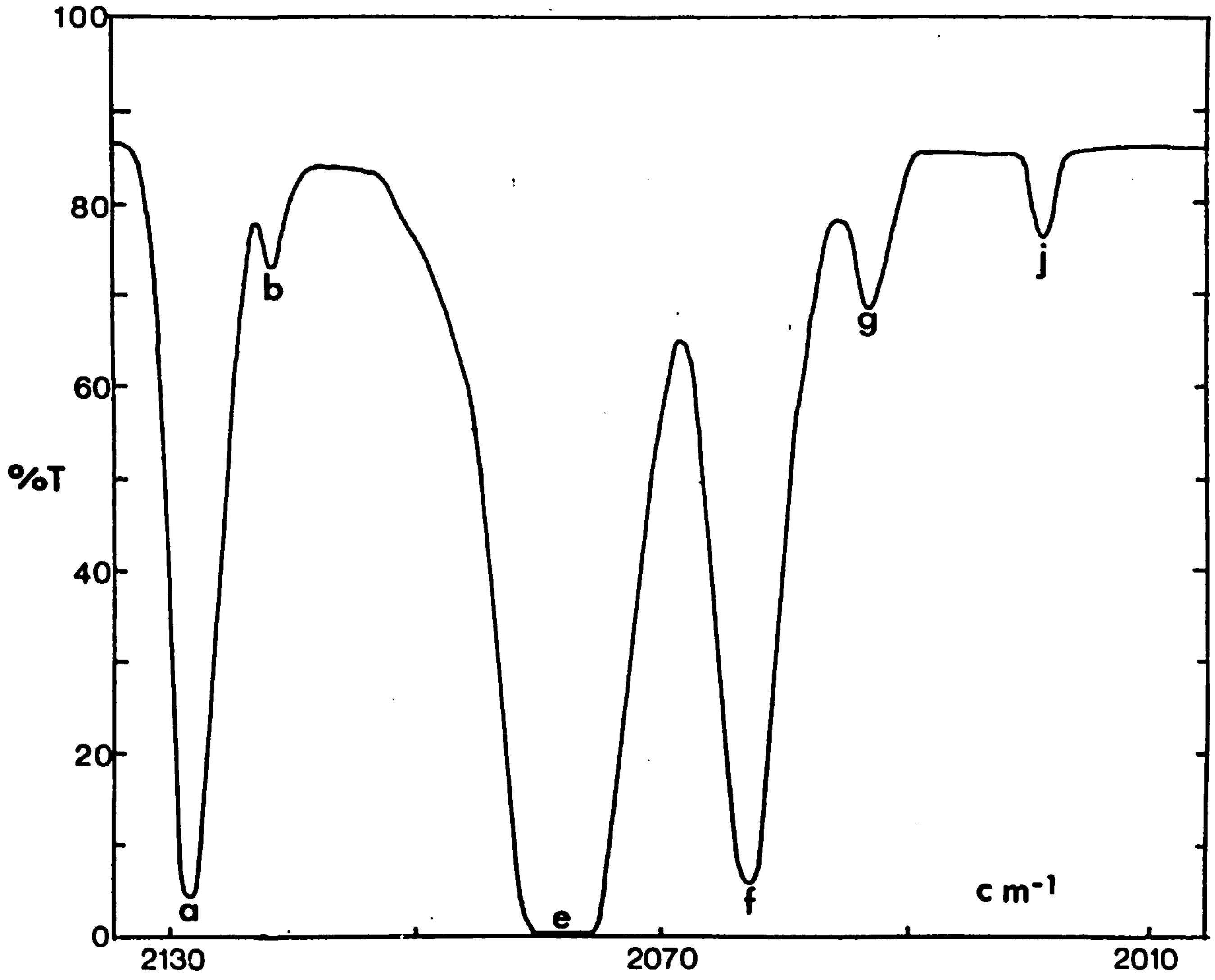

Figure 8.-Spectrum of *cis*-Fe(CO)$_4$I$_2$ with natural abundance of ^{13}C (cyclohexane solution).

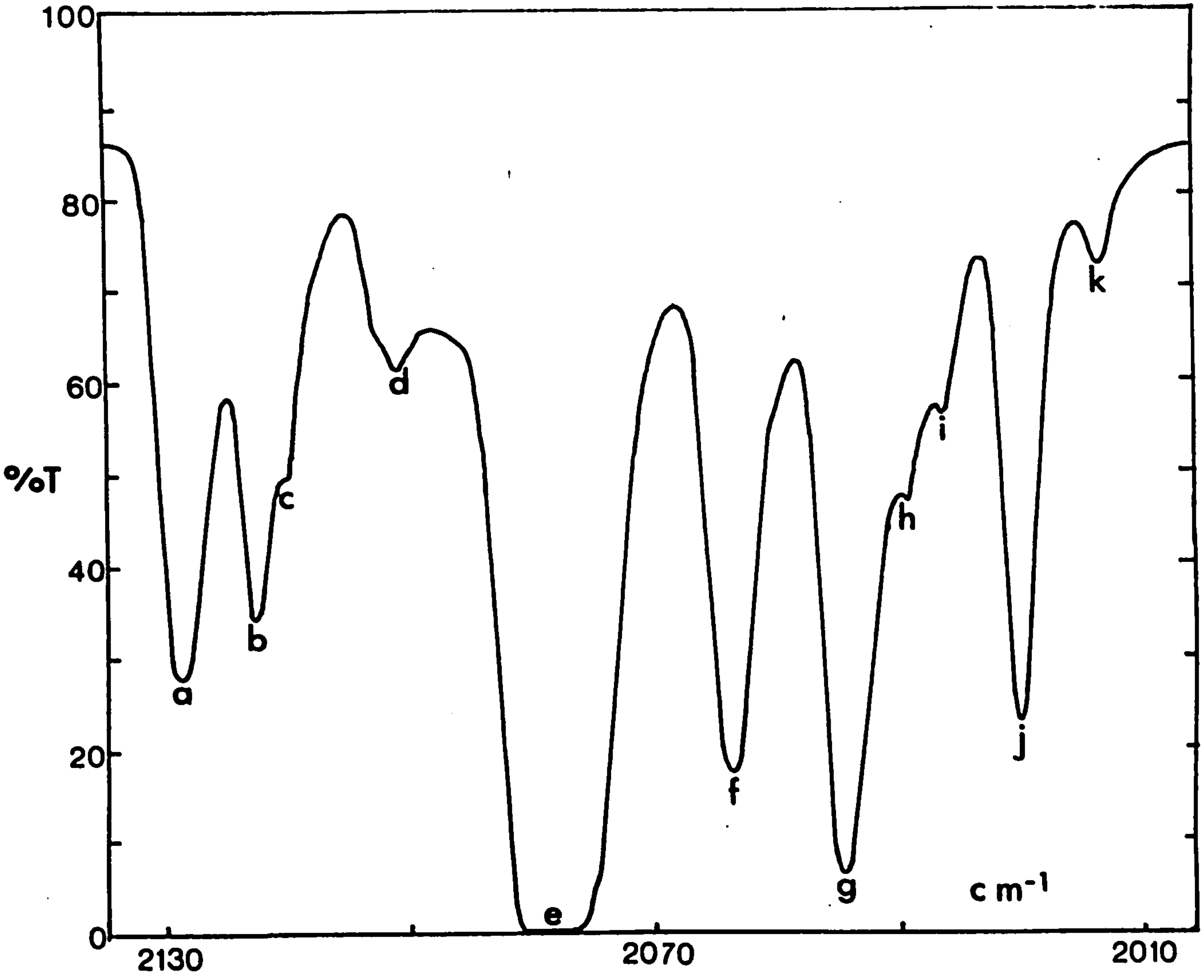

Figure 9.-Spectrum of *cis*-Fe(CO)$_4$I$_2$ after 3hr exchange with 50% ^{13}C-enriched CO (cyclohexane solution).

TABLE I OBSERVED SPECTRA IN THE CO STRETCHING REGION OF *cis*-$Fe(CO)_4X_2$ (X = I, Br) IN CYCLOHEXANE. CALCULATION OF FORCE CONSTANTS TO ASSIGN THE OBSERVED SPECTRA

		ν(CO) (cm^{-1})						
		cis-$Fe(CO)_4I_2$ [a]				*cis*-$Fe(CO)_4Br_2$ [b]		
Molecule and Symmetry	Vib. Assignment	Observed	Band Designation	Input	Calcd.	Observed	Input	Calcd.
	$\underline{a}_1^{(2)}$	$2128._4$	a	2128.4	2128.5	$2148._6$	2148.6	2148.7
all-^{12}CO	$\underline{a}_1^{(1)}$	-		-	2080.8	$2098._6$	2098.6	2098.2
C_{2v}	$\underline{b}_1$	$2083._5$	e	2083.5	2083.6	$2108._7$	2108.7	2108.5
	$\underline{b}_2$	$2060._0$	f	2060.0	2059.9	$2074._4$	2074.4	2073.3
mono-^{13}CO	$\underline{a}'$	$2118._8$	b	2118.8	2118.7	$2138._7$	2138.7	2138.5
axial sub-	$\underline{a}'$	-		-	2081.3	-	-	2100.3
stitution	$\underline{a}'$	$2046._3$	g	2046.3	2046.2	$2069._0$	2069.0	2069.4
C_s	$\underline{a}''$	-		-	2059.9	-	-	2073.3
	$\underline{a}'$	-		-	2125.2	-	-	2145.9
mono-^{13}CO	$\underline{a}'$	-		-	2073.9	$2090._5$	-	2090.1
radial sub-stitution	$\underline{a}''$	-		-	2083.6	-	-	2108.5
C_s	$\underline{a}'$	$2023._9$	j	2023.9	2024.0	$2036._3$	2036.3	2037.7

TABLE I(Cont'd)

di-^{13}CO 1, 2-substitution C_{2v}	$\underline{a}_1^{(2)}$	$2100._5$	d	-	2104.3	-	-	2121.2
	$\underline{a}_1^{(1)}$	-		-	2057.9	-	-	2078.1
	$\underline{b}_1$	$2034._1$	i	-	2037.3	-	-	2061.6
	$\underline{b}_2$	-		-	2039.9	-	-	2073.3
di-^{13}CO 1, 3-substitution C_1	$\underline{a}$	$2115._7$sh	c	-	2114.3	$2131._4$	-	2135.1
	$\underline{a}$	-		-	2075.3	-	-	2092.9
	$\underline{a}$	-		-	2047.1	-	-	2069.7
	$\underline{a}$	-		-	2023.3	-	-	2037.3
di-^{13}CO 3, 4-substitution C_{2v}	$\underline{a}_1^{(2)}$	-		-	2122.3	-	-	2143.5
	$\underline{a}_1^{(1)}$	$2038._7$sh	h	-	2040.5	$2055._4$	-	2056.5
	$\underline{b}_1$	-		-	2083.6	-	-	2108.5
	$\underline{b}_2$	$2013._9$	k	-	2014.2	$2026._3$	-	2027.2

[a] Calculated force constants: k_1 = 17.407, k_2 = 17.813, k_c = 0.174, $k_{c'}$ = 0.273, and k_t = 0.283 (mdyn/Å)

[b] Calculated force constants: k_1 = 17.652, k_2 = 18.212, k_c = 0.172, $k_{c'}$ = 0.295, and k_t = 0.261 (mdyn/Å)

The assignment shown in Table I for the fundamentals of all-^{12}CO *cis*-Fe(CO)$_4$I$_2$ was originally proposed by Abel and Butler[60] on the basis of force constant calculations using the Cotton-Krainhanzel "approximate" force field. This assignment was supported by the force constant calculations of Johnson *et al.*[47] in their C^{18}O exchange study. Because of the similarity in the reduced masses of ^{13}CO and C^{18}O, similar isotopic shifts are observed when a ^{12}CO group in a metal carbonyl is substituted by either of these molecules. As a consequence, the frequencies observed in this work and in that by Johnson *et al.*[47] differ by only about 1cm^{-1}, and the vibrational assignments for the various ^{13}CO substituted species present during ^{13}CO exchange are identical to those for the C^{18}O exchange.

The assignment of the observed modes proceeds as follows. Since a number of new bands appear between the fundamental at 2128.4cm^{-1} and the next fundamental at 2083.5cm^{-1}, this designates the former as arising from a vibration involving more than two CO groups. It therefore must be an $\underline{a}_1$ vibration because the symmetric modes are the only ones in which more than two CO groups participate. The isotopic band at 2023.9cm^{-1} must arise from the all-^{12}CO fundamental at 2060.0cm^{-1} ($\Delta\nu$ = 36.1cm^{-1}) since the next fundamental at 2083.5cm^{-1} is too far removed ($\Delta\nu > 50$cm^{-1}). Therefore, the band at 2046.3cm^{-1} derives from the parent mode at 2083.5cm^{-1} ($\Delta\nu$ = 37.2cm^{-1}). These two shifts are too large to arise from symmetric vibrations involving more than one CO group; thus bands e and f must be the $\underline{b}_1$ and $\underline{b}_2$ modes. Their relative order can only be determined through force constant calculations. Our initial assignment differs slightly from that of Johnson *et al.*[47] in that a new isotopic band at 2075cm^{-1} was not observed, and it was therefore impossible to conclude that the $\underline{a}_1$ mode of the all-^{12}CO molecule was degenerate with the $\underline{b}_1$ or $\underline{b}_2$ mode at 2083.5cm^{-1}. This degeneracy had to be confirmed through the force constant calculations.

In order to test the assignments, a set of approximate force constants were adjusted by the iterative computer program to fit the observed frequencies which had been assigned to the all-^{12}CO and mono-^{13}CO axial and radial substituted* *cis*-$Fe(CO)_4I_2$ molecules. The optimum calculated force constants and the associated frequencies are shown in Table I. In their study, Johnson *et al.*[47] found that if the assignments of the $\underline{b}_1$ and $\underline{b}_2$ modes of the all-^{12}CO molecule were reversed, then the agreement between the observed and calculated frequencies was again very close, but the values of k_1 and k_2, and k_c,and k_t were reversed. This was also found to be the case in this work. However, as Johnson *et al.*[47] pointed out, such a reversal results in $k_1 > k_2$, and since previous studies on $Mn(CO)_5X$[18,20,23] and $Re(CO)_5X$[18,23] have shown that $k_2 > k_1$ (where anharmonicity corrections are ignored), it seems reasonable to assume that a similar situation should exist for *cis*-$Fe(CO)_4X_2$. In any event, for the purposes of the present discussion it will be assumed that $k_2 > k_1$, even though this has not been definitely established.

It can be seen from Table I that the $\underline{a}_1^{(1)}$ frequency for the all-^{12}CO molecule is calculated to be 2080.8cm^{-1}, indicating, as has previously been suggested,[47,59,60] that this mode is accidentally degenerate with the $\underline{b}_1$ mode at 2083.5cm^{-1}. (Using a very high resolution spectrometer Pankowski and Bigorgne[62] have been able to resolve this band into

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* The terms axial and radial refer to the CO groups in Figure 6 in positions 1 and 2, and in positions 3 and 4, respectively.

two components separated by 1.6cm^{-1}.) The experimental frequencies which were not used as input were predicted to within 4cm^{-1}, *i.e.* within the error range expected when using frequencies uncorrected for anharmonicity[51,52] and the CO-factored force field. The good agreement between the observed and predicted frequencies serves as an independent check on the validity of the assignments.

The observed CO stretching frequencies of *cis*-$Fe(CO)_4Br_2$ in cyclohexane after ^{13}CO exchange (2.5 hr) and the proposed vibrational assignments are shown in Table I. In this case it was possible to resolve all four fundamentals of the all-^{12}CO molecule. The assignment given for these fundamentals was originally proposed by Abel and Butler.[60] It has recently been supported by the force constant calculations of Johnson *et al.*[47] involving the frequencies of the weak absorptions in the spectrum which these workers attributed, without any direct proof, to naturally occurring ^{13}CO molecules. We have now experimentally verified through enrichment with ^{13}CO that these weak absorptions are in fact due to ^{13}CO substituted molecules present in natural abundance. In this study, it was also possible to observe two new absorptions in the spectrum of the enriched sample which could be unequivocably assigned to di-^{13}CO substituted molecules. The natural abundance of these molecules is far too low for their absorptions to be detected in the absence of enrichment. The force constants for *cis*-$Fe(CO)_4Br_2$ were obtained by the same procedure as that used for the di-iodide. The assignment of the four fundamentals of the all-^{12}CO molecule shown in Table I was selected because it is similar to that determined for the di-iodide and it leads to a set of force constant data which satisfies our assumption that $k_2 > k_1$ (as before, there is close agreement between the observed and calculated frequencies if the assignments of the $\underline{b}_1$ and $\underline{b}_2$ modes and the values of k_1 and k_2, and k_c, and k_t are reversed). The optimum calculated force constants for the assignment chosen and the associated frequencies for the all-^{12}CO and the various mono- and di-^{13}CO substituted molecules are given in Table I. The observed frequencies of the di-^{13}CO species were not used as input and were predicted to within 4cm^{-1}, indicating the validity of the proposed assignments.

In Table II the force constants for the *cis*-$Fe(CO)_4X_2$ molecules from the present work are compared with those reported by Johnson *et al.*[47] At first sight there appear to be some quite significant differences, but it should be remembered that there are a number of factors which can influence the values of the force constants. For example, when different sets of input frequencies were used for either molecule, the remaining frequencies were predicted to within the usual range of error, but the calculated force constants differed from those shown in Table II by up to ±0.025 mdyn/Å. The interaction constant, k_c, ,seemed to be particularly affected by the choice of input frequencies. It has become increasingly evident recently from (1) calculations on the effect of small frequency changes on the force constants,[66] (2) the effect of including low-frequency modes in the force field,[51,52] and (3) anharmonicity corrections on the observed frequencies,[51,52] that the correspondence of observed and calculated frequencies of metal carbonyl derivatives does not mean that the associated force constants have any fundamental significance. Therefore, it is felt unwise to discuss either the differences in the force constant data obtained in the two studies, or the apparent

TABLE II. CALCULATED FORCE CONSTANTS FOR

cis-$Fe(CO)_4X_2$ (X =I, Br) (mdyn/Å)

	k_1	k_2	k_c	$k_{c'}$	k_t
		cis-$Fe(CO)_4I_2$			
This work	17.407	17.813	0.174	0.273	0.283
Johnson *et al.*	17.451	17.860	0.160	0.280	0.300
		cis-$Fe(CO)_4Br_2$			
This work	17.652	18.212	0.172	0.295	0.261
Johnson *et al.*	17.617	18.290	0.098	0.220	0.337

trends in the force constants of the compounds themselves.

ii. Stereochemistry of the ^{13}CO Exchange Reaction of *cis*-$Fe(CO)_4I_2$

The exchange of radioactive ^{14}CO with *cis*-$Fe(CO)_4I_2$ has been studied by Wojcicki and Basolo.[17] The kinetic data indicated that all four CO groups exchanged at the same rate and that the rate depended on the concentrations of the metal carbonyl and ^{14}CO. Consistent with the latter observations, it was suggested that the exchange takes place by a direct displacement process. However, recently, Cohen and Basolo[64] reported data for the substitution reactions of *cis*-$Fe(CO)_4X_2$ (X = I and Br) with a variety of ligands, L, to yield the monosubstituted products $Fe(CO)_3LX_2$. The rate of formation of $Fe(CO)_3LX_2$ did not depend on the concentration of L, but the reaction was light catalysed and was inhibited by the addition of X_2. It was suggested that the mechanism for this reaction involved the initial formation of $Fe(CO)_4$, followed by its reaction with L and then LX_2 to generate the product $Fe(CO)_3LX_2$. Cohen and Basolo also studied the inhibitory effect of X_2 on the ^{14}CO exchanges with *cis*-$Fe(CO)_4X_2$ and found that the rates were markedly affected. I_2 was particularly effective in inhibiting the rate of exchange of *cis*-$Fe(CO)_4I_2$ since the I_2 concentration had only to equal that of ^{14}CO in order to reduce the rate by 85%. Free Br_2 inhibited the ^{14}CO exchange of *cis*-$Fe(CO)_4Br_2$ by 50% when $[Br_2]$ was 350 times $[^{14}CO]$.

Basolo and Cohen explained that it was the inhibitory effect of X_2 which led to the exchange rates being $[^{14}CO]$ dependent, even though the reactions were *not* S_N2 displacement processes. The mechanism which they suggested is analogous to that for the reactions with ligands, L, and is shown below:

$$\begin{array}{lcl} \textit{cis}\text{-Fe(CO)}_4X_2 & \rightleftarrows & \text{Fe(CO)}_4 + X_2 \\ \text{Fe(CO)}_4 + {}^{14}\text{CO} & \rightarrow & \text{Fe(CO)}_4({}^{14}\text{CO}) \\ \text{Fe(CO)}_4({}^{14}\text{CO}) & \rightarrow & \text{Fe(CO)}_3({}^{14}\text{CO}) + \text{CO} \\ \text{Fe(CO)}_3({}^{14}\text{CO}) + X_2 & \rightarrow & \textit{cis}\text{-Fe(CO)}_3({}^{14}\text{CO})X_2 \end{array} \tag{38}$$

In any series of experiments if the $[X_2]$ due to contamination (*e.g.* I_2 co-sublimes with *cis*-$Fe(CO)_4I_2$) or the steady state $[X_2]$ is constant, then an increase in $[^{14}CO]$ will, by a competition effect, increase the opportunity of a given $Fe(CO)_4$ molecule to react with a ^{14}CO rather than with an X_2 molecule. Thus, the second order ^{14}CO exchange was really a set of competition experiments with a constant $[X_2]$.

Provided that we are correct in assuming $k_2 > k_1$, bands g and j in Figures 8 and 9 are characteristic of mono-^{13}CO axial and radial substituted *cis*-$Fe(CO)_4I_2$, respectively. The ratio of the absorbances of these bands remained reasonably constant throughout the exchange with ^{13}CO (Table III). Since it is evident from Figure 9 that the exchange had not progressed very much beyond the mono-^{13}CO substitution stage in 3 hr, it appears that the axial and radial CO groups exchange at qualitatively the same rate. This is in accord with the radiocarbon monoxide studies discussed above.

iii. Potential Energy Distribution

The potential energy distribution for *cis*-$Fe(CO)_4I_2$ and *cis*-$Fe(CO)_4Br_2$ are shown in Table IV. The one important conclusion which

TABLE III. RATIO OF ABSORBANCES OF BANDS g AND j IN THE SPECTRUM OF *cis*-$Fe(CO)_4I_2$ AT DIFFERENT TIMES THROUGHOUT THE EXCHANGE WITH ^{13}CO

Time (min)	A_g/A_j
0	2.00
1.5	2.09
8.0	2.00
20.0	1.85
25.0	1.88
45.0	1.82
60.0	1.90
95.0	1.96

TABLE IV. POTENTIAL ENERGY DISTRIBUTION.[a]

cis-Fe(CO)$_4$I$_2$

Band	k_1	$k_{c'}$	k_c	k_2	k_t
a	0.2320	0.0036	0.0164	0.7363	0.0117
e				1.0162	-0.0162
f	1.0159	-0.0159			
b	0.3296	0.0052	0.0168	0.6412	0.0072
g	0.0508	0.0008	-0.0045	0.9600	-0.0071
j	0.9979	-0.0082	-0.0021	0.0122	0.0002
			cis-Fe(CO)$_4$Br$_2$		
a	0.1859	0.0031	0.0145	0.7851	0.0112
$\underline{a}_1^{(1)}$	0.7981	0.0133	-0.0154	0.2011	0.0029
e				1.0145	-0.0145
f	1.0170	-0.0170			
b	0.2534	0.0042	0.0149	0.7206	0.0068
g	0.0755	0.0013	-0.0056	0.9341	-0.0053
j	1.0017	-0.0094	-0.0017	0.0093	0.0001

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[a] The band designations have been taken from Table I on p. 119.

may be drawn from this table is the contribution of the symmetric stretching of the mutually *cis* CO groups to the high frequency symmetric vibration of the mutually *trans* CO groups. It is seen that this contribution is higher in the iodo- than in the bromo-compound; this result substantiates that of Johnson *et al.*[47] The result is in agreement with the observation that for the iodo-compound the intensity of the high frequency $\underline{a}_1$ vibration is greater than that for the corresponding bromo-derivative.[58,60] This follows from the fact that if there was no mixing at all, the intensity of the upper frequency mode would be very small since the symmetric stretch of two CO groups *trans* to one another would produce a very small, or non-existent, dipole moment change. As Johnson *et al.*[47] pointed out, this is not the only factor influencing the intensity since steric distortions, etc. also play a part in this effect.

CHAPTER V ANALYSIS OF THE SPECTRA OF THE ISOTOPIC SUBSTITUTION REACTIONS OF *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$)

A. INTRODUCTION

As a follow-up of the isotopic exchange studies on the $Mn(CO)_5X$[18,20] complexes, the exchange reactions of the *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$) complexes have been investigated. These molecules are known to substitute one of their CO groups in favour of another ligand; with the order of reactivity being $PPh_3 > AsPh_3 > SbPh_3$.[67]

From an investigation of the isotopic substitution reactions of these complexes it has been possible to assign the CO stretching modes in the all-^{12}CO and the various isotopically substituted species, and to calculate the force constants associated with these vibrations. By examining the CO substitution in *cis*-$Mn(CO)_4(PPh_3)Br$ it has also been possible to arrive at some qualitative conclusions as to the existence of stereospecific substitution in these complexes. The complexes having L = $AsPh_3$ and $SbPh_3$ were also found to replace L with CO giving $Mn(CO)_5Br$. The reaction of *cis*-$Mn(CO)_4(SbPh_3)Br$ with $C^{18}O$ was therefore examined in detail to determine if any rearrangement of the CO groups had taken place during, or after, the formation of $Mn(CO)_5Br$.

B. RESULTS AND DISCUSSION

i. Assignment of the Observed Spectra

The *cis*-Mn(CO)$_4$LX complexes are presumed to possess the structure shown in Figure 10. The idealized symmetry is C_s, and four CO stretching vibrations of symmetry 3a' + a" are expected. These are also shown schematically in Figure 10.

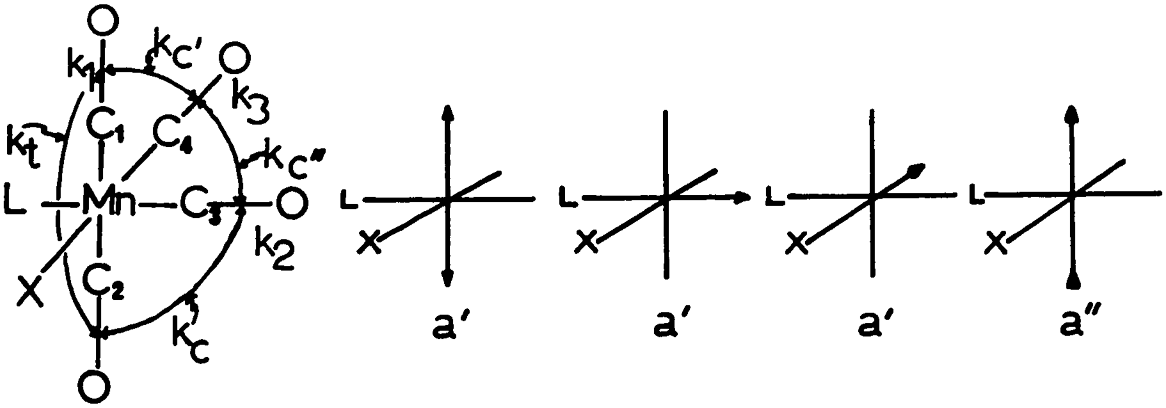

Figure 10.-Idealized structure and Cotton-Kraihanzel parameters for *cis*-M(CO)$_4$LX. Symmetry coordinates.

The spectra recorded for the reaction with L = PPh$_3$ provided the maximum amount of data because the reaction proceeded towards equilibrium at the fastest rate; it will therefore be discussed in detail. The infrared frequencies of the reaction mixture at various times are given in Table V along with their relative intensities. Sample spectra are shown in Figure 11.

From the table a number of conclusions may be immediately arrived at:

1. The bands observed between 2080 and 2040cm^{-1} must all be isotopic

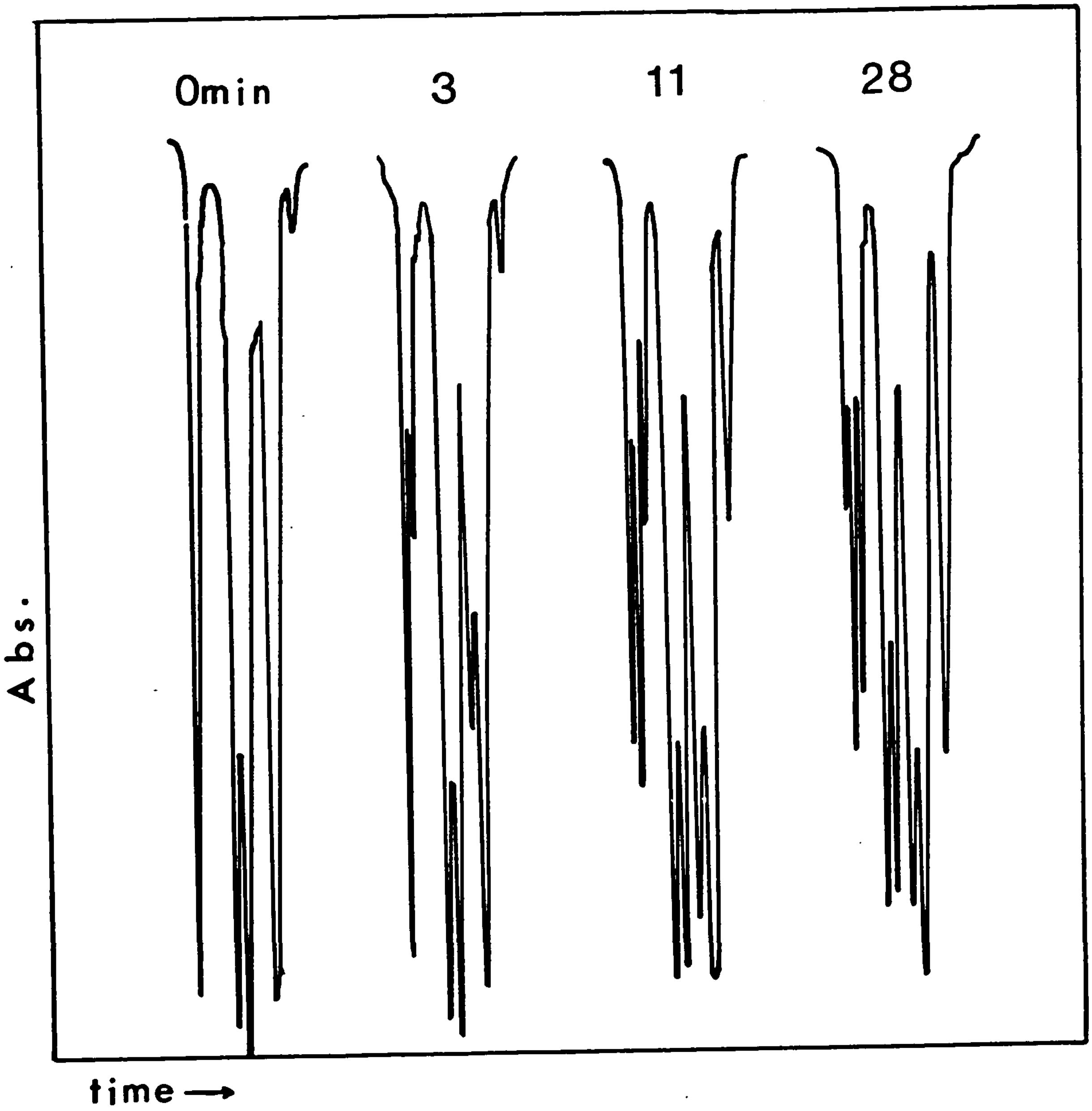

Figure 11.-Sample spectra of the $C^{18}O$ exchange of *cis*-$Mn(CO)_4(PPh_3)Br$ (cyclohexane solution).

TABLE V. INFRARED FREQUENCIES AND INTENSITIES FOR THE REACTION

cis-$Mn(CO)_4(PPh_3)Br + C^{18}O$ AT 35° IN *n*-HEXANE

Frequency cm^{-1}	time (min)											Band designation
	zero	3	11	20	28	39	55	74	122	180	260	
2089.2	vs	vs	m	mw	w	w	w	w	vw	vw	vvw	a
2077.0		w	m	m	m	m	m	m	m	mw	mw	b
2063.0			w	m	m	m	m	m	m	mw	mw	c
2058.6						mw	m	m	m	m	mw	d
2048.7										vw	w	e
2042.6										vw	w	f
2023.6	vs	vs	vs	s	s	s	ms	ms	ms	m	m	g
2006.0	vs	vs	vs	s	s	ms	ms	ms	ms	ms	ms	h
1979.4		m	s	s	s	s	s	s	s	s	s	i
1960.2	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	j
1919.3		vw	w	m	m	ms	ms	ms	ms	ms	ms	k

vibrations associated with the CO group(s) whose $C^{12}O^{16}$ fundamental is at $2089.2cm^{-1}$ since no other parent fundamental exists above $2025cm^{-1}$.

2. The band at $1919.3cm^{-1}$ must be a derivative of the fundamental at $1960.2cm^{-1}$. This gives a shift of $41.1cm^{-1}$, while for the next closest fundamental at $2006.0cm^{-1}$ the shift is $87.7cm^{-1}$. This last figure is much too high; the maximum shift for bands around $2000cm^{-1}$ is predicted by the Teller-Redlich rule to be approximately $50cm^{-1}$.

3. The band at $1979.4cm^{-1}$ must arise from either the parent fundamental at 2023.6 or $2006.0cm^{-1}$, the shift in each case being 44.2 and $26.6cm^{-1}$, respectively. We cannot therefore make any *a priori* decision as to the source of this band.

4. The three bands at 2077.0, 1979.4, and $1919.3cm^{-1}$ are probably all due to monosubstitution products since they are the first to make their appearance.

Following this preliminary build-up, the fundamentals of the parent complex may now be assigned. A number of facts suggest that the high frequency mode at $2089.2cm^{-1}$ is the symmetric vibration of the two *trans*-CO groups, 1 and 2. Firstly, the large number of isotopic bands, five at least, arising from this fundamental can only be explained if the band is attributed to a vibration associated with more than two CO groups. This eliminates its assignment as the $\underline{a}''$ vibration. Secondly, the initial shift $\Delta\nu = \nu_a - \nu_b = 12.2cm^{-1}$ is too small to arise from a totally substituted vibration. As a comparison, the shifts observed for the axial stretching vibrations (involving one CO group) in $Mn(CO)_5X$ are of the order of $40cm^{-1}$,[18,20] while those for the symmetric vibrations (involving two CO groups) in *cis*-$Fe(CO)_4X_2$ are in the range $10\text{-}15cm^{-1}$.[47,63] Thirdly, the pattern of increase and decrease in absorbance of the bands at 2089.2, 2077.0, and 2063.0cm^{-1} (bands a, b, and c, respectively) with respect to one another points clearly to the fact that a reaction of the type A → B → C is taking place. This sequence can be explained by assuming that band a is the fundamental stretch connected with the *trans*-$C^{16}O$ groups, band b is due to the monosubstituted $C^{18}O$ derivative, and band c to the disubstituted $C^{18}O$ derivative. The frequency shifts, 12.2 and 26.0cm^{-1}, of bands b and c, respectively, from the parent carbonyl band a also point to the same conclusion.*

An examination of the relative intensities of the bands at 2023.6 and 2006.0cm^{-1} (bands g and h, respectively,) also leads to some conclusions concerning the assignment of the fundamentals. Initially, band h is more intense than band g, but after only 11 min, band g is observed to be the slightly more intense one, and this persists until, in the spectrum taken at 39 min the intensities are approximately equal, and from then on the original intensity order is restored. The band at 1979.4cm^{-1} increases at a very fast rate which is not matched by the decrease in intensity of the band at 2023.6cm^{-1}, it is therefore assigned as arising from the fundamental at 2006.0cm^{-1}. From a comparison of the very fast initial rates of disappearance of bands a and h and the rates of appearance of their isotopic bands b and i, it appears that all these frequencies are associated with carbonyl groups in the same position, *viz.* those *trans*- to one another. Band h can therefore be assigned to the a" mode. Even when the high frequency

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* It has recently been established[68] that the band at 2090cm^{-1} in the laser Raman spectrum of *cis*-$Mn(CO)_4(PPh_3)Br$ in chloroform solution is polarized, indicating a totally symmetric vibration.

band at 2089.2cm^{-1} (band a) has virtually disappeared, band h at 2006.0cm^{-1} still has an appreciable intensity. This is most probably due to the fact that one of the isotopic vibrations associated with the fundamental at 2023.6cm^{-1} is accidentally degenerate with the a" mode. This suggestion will be confirmed by the normal coordinate calculations to be described later.

The assignment of band h to the a" mode also explains the intensity pattern discussed above. The initial higher intensity of band h compared to that of band g is reversed when the two CO groups *trans* to one another exchange at a rate faster than that for the other CO groups. This is expected from the bonding in these complexes as detailed above. When exchange equilibrium is reached for these two carbonyl groups, band h stops decreasing in intensity, while band g will go on decreasing until the exchange of the carbonyl group giving rise to it also reaches equilibrium, thus accounting for the return to the original intensity order.

By elimination, band g and j are therefore the a' modes of the CO groups *trans* to either PPh_3 or Br. No distinction can be made on the basis of the isotopic exchange, and it is necessary to have recourse to the oft-invoked argument (*e.g.* ref. 50) that the CO *trans* to the halogen is expected to have the lowest force constant, in order to differentiate between the two assignments. Thus band g (2023.6cm^{-1}) is assigned to the vibration of the CO group *trans* to PPh_3, while band j (1960.2cm^{-1}) is assigned to the vibration of the CO group *trans* Br. It should be emphasized that the three a' modes are most likely quite mixed.

The fact that the intensity of the band at 1960.2cm^{-1} (band j) remains virtually unchanged until well into the reaction can be explained by two factors: (1) The rate of disappearance of this band is expected to be slower than that of the other bands because the CO group *trans* to Br is more strongly attached to the central metal than the others; (2) the a" mode of the *trans*-disubstituted isotopic species is accidentally degenerate with it.

The proposed assignment of the fundamentals agrees with that given by Angelici[69] for a related molecule, *cis*-$Mn(CO)_4(PPh_3)I$. The basis of his assignment was that the separation between the absorptions due to the symmetric and antisymmetric modes of the CO groups *trans* to one another would be the same in *cis*-$Mn(CO)_4I_2^-$ and *cis*-$Mn(CO)_4(PPh_3)I$. Thus the bands observed at 2084 and 2006cm^{-1} were assigned to the a' and a" vibrations, respectively, of the *trans*-CO groups. The band at lowest frequency (1962cm^{-1}) was then assigned to the CO *trans* to I leaving the band at 2021cm^{-1} to be assigned to the CO *trans* to PPh_3.

In the reactions of *cis*-$Mn(CO)_4(SbPh_3)Br$ and *cis*-$Mn(CO)_4(AsPh_3)Br$ with $C^{18}O$ it was observed that apart from the isotopic exchange, another reaction was taking place. This was found to be the formation of isotopically substituted $Mn(CO)_5Br$ by replacement of the ligands with carbon monoxide.

$$\textit{cis}\text{-}Mn(CO)_4LBr \rightarrow \begin{cases} \textit{cis}\text{-}Mn(CO)_3(C^{18}O)LBr + CO \\ Mn(CO)_4(C^{18}O)Br + L \end{cases} \qquad (39)$$

This reaction will be discussed in more detail in Section iii.b. below. The fundamental and isotopic frequencies observed for the two tetracarbonyl complexes together with the suggested assignments are given in Table VI.

TABLE VI. OBSERVED SPECTRA IN THE CO STRETCHING REGION OF *cis*-$Mn(CO)_4LBr$ ($L = SbPh_3, AsPh_3$) IN CYCLOHEXANE. CALCULATION OF FORCE CONSTANTS TO ASSIGN THE OBSERVED SPECTRA

		$\nu(CO)$ (cm^{-1})					
		cis-$Mn(CO)_4(SbPh_3)Br$[a,b,c]				*cis*-$Mn(CO)_4(AsPh_3)Br$[c,d]	
Molecule and Symmetry	Vib. Assignment	Observed	Input	Calcd.	Band Designation	Observed and Input[e]	Calcd.
Unsubstituted C_s	*a'*	$2084._7$	2084.7	2084.7	a	$2088._3$	2088.2
	a'	$2018._3$	2018.3	2018.3	c	$2019._3$	2019.3
	a'	$1957._5$	1957.5	1957.5	g	$1959._6$	1959.6
	a"	$2006._7$	2006.7	2006.7	d	$2008._3$	2008.3
Mono-$C^{18}O$ in positn. 1 C_1	*a*	$2072._8$	2072.8	2072.8	b	$2075._7$	2075.8
	a	-	-	2016.5		-	2017.8
	a	$1975._2$	1975.2	1975.2	f	$1978._3$	1978.3
	a	-	-	1953.8		-	1954.4

Mono-$C^{18}O$	a'	-	-	2079.0		-	2083.9
in positn. 3	a'	$1984._4$	1984.4	1984.4	e	-	1985.1
C_s	a'	$1948._4$	-	1948.3	h	-	1949.4
	a"	-	-	2006.7		-	2008.3
Mono-$C^{18}O$	a'	-	-	2080.6		-	2082.9
in positn. 4	a'	-	-	2017.7		-	2018.6
C_s	a'	$1914._6$	1914.6	1914.6	i	$1917._9$	1917.9
	a"	-	-	2006.7		-	2008.3

[a] Calculated force constants: $k_1 = 16.718$, $k_t = 0.458$, $k_c = 0.237$, $k_{c'} = 0.360$, $k_2 = 16.572$, $k_{c''} = 0.415$, $k_3 = 15.720$ (mdyn/Å)

[b] Calculated force constants using set (3) as discussed in the text: $k_1 = 16.718$, $k_t = 0.457$, $k_c = 0.237$, $k_{c'} = 0.360$, $k_2 = 16.573$, $k_{c''} = 0.417$, $k_3 = 15.721$ (mdyn/Å)

[c] $Mn(CO)_5Br$ modes were observed at 2050.3 and 1996.2cm^{-1}

[d] Calculated force constants: $k_1 = 16.751$, $k_t = 0.465$, $k_c = 0.201$, $k_{c'} = 0.426$, $k_2 = 16.540$, $k_{c''} = 0.423$, $k_3 = 15.823$ (mdyn/Å)

[e] Also observed and used as input was a band at 2060.0cm^{-1} assigned to the di-$C^{18}O$ 1,2-substituted molecule. This band was calculated at 2059.9cm^{-1}

ii. Force Constant Calculations

Using the high-frequency separation approximation, seven independent force constants may be used to construct the force field. These are defined in Figure 10. A normal coordinate treatment provides the symmetrized F matrices:

$$F_{\underline{a}'} = \begin{bmatrix} k_1 + k_t & \sqrt{2}.k_c & \sqrt{2}.k_{c'} \\ & k_2 & k_{c''} \\ & & k_3 \end{bmatrix}$$

$$F_{\underline{a}''} = [\ k_1 - k_t\ ]$$

In the case of *cis*-$Mn(CO)_4(PPh_3)Br$, eight of the eleven observed frequencies, were used as input to calculate the seven force constants. The eight frequencies chosen were those that could be assigned with the greatest confidence, namely a, b, c, g, h, i, j, and k. The other frequency assignments were obtained *via* back-calculation. The calculated spectra of *cis*-$Mn(CO)_{4-n}(C^{18}O)_n(PPh_3)Br$ and the associated force constants are given in Table VII. As predicted, the 1, 2-disubstituted and 1, 2, 4-trisubstituted species have calculated

TABLE VII. CALCULATED FREQUENCIES AND FORCE CONSTANTS FOR

cis-$Mn(C^{16}O)_{4-n}(C^{18}O)_n(PPh_3)Br$, n = 0 - 4.

Position of sub-stitution	Frequency[a]	Symmetry	Position of sub-stitution	Frequency	Symmetry
0	[2089.1]	a'	1,4	2069.7	a
	[2023.6]	a'		2021.7	a
	[1960.5]	a'		1974.6	a
	[2006.0]	a"		1916.3	a
1	[2077.1]	a	3,4	2078.2	a'
	2021.7	a		1980.7	a'
	[1979.4]	a		1917.6	a'
	1952.0	a		2006.0	a"
3	2084.8	a'	1,2,3	2050.8	a'
	1984.2	a'		1974.9	a'
	1955.2	a'		1948.9	a'
	2006.0	a"		1957.7	a"
4	2082.5	a'	1,2,4	2053.5	a'
	2023.6	a'		2007.8	a'
	[1919.3]	a'		1914.4	a'
	2006.0	a"		1957.7	a"
1,2	[2062.2]	a'	2,3,4	2063.4	a
	2010.7	a'		1985.5	a
	1950.6	a'		1969.6	a
	1957.7	a"		1915.0	a
1,3	2071.2	a	1,2,3,4	2038.7	a'
	1989.9	a		1974.8	a'
	1970.1	a		1913.3	a'
	1950.1	a		1957.7	a"

$k_1 = 16.698$, $k_t = 0.450$, $k_c = 0.189$, $k_{c'} = 0.501$, $k_2 = 16.646$, $k_{c''} = 0.356$, $k_3 = 15.882$ (mdyn/Å)

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[a] The frequencies in parentheses were used as input.

frequencies at 2010.7 and 2007.8cm^{-1}, respectively, *i.e.* close to the parent fundamental vibration at 2006.0cm^{-1}, thus accounting for the latter's lack of intensity change during the later stages of the exchange reaction.

For *cis*-$Mn(CO)_4(SbPh_3)Br$, three sets of frequencies were adjusted: (1) a, b, c, d, e, f, g, and i, (2) a, b, c, d, f, g, h, and i, with band h arising from monosubstitution in position 1, and (3) same as in (2) but with band h arising from monosubstitution in position 3. By using the first set, band h (which was not used as input) was calculated to be 1948.3cm^{-1} (observed at 1948.4cm^{-1}). The third set provided a calculated value of band e at 1984.2cm^{-1} (observed at 1984.4cm^{-1}), and force constants almost identical to those calculated using the first set. On the other hand the second set gave a calculated value of 1981.8cm^{-1} for band e and a larger error in the other calculated frequencies as compared to input values. The final assignment and associated force constants are given in Table VI, for both *cis*-$Mn(CO)_4(SbPh_3)Br$ and *cis*-$Mn(CO)_4(AsPh_3)Br$.

iii. Stereochemical Considerations

a. In *cis*-$Mn(CO)_4LBr$ complexes

Direct comparison of the intensities of the bands at 2089.2 and 2023.6cm^{-1} for *cis*-$Mn(CO)_4(PPh_3)Br$ indicates that the carbonyl groups giving rise to them exchange at very different rates, with the band at 2089.2cm^{-1} disappearing much faster, as expected. Unfortunately, no such direct comparison may be made with the band at 1960.2cm^{-1} because of the overlap with the isotopic CO band. A rough idea may be gained, however, by comparing the rates of appearance of the isotopic bands arising from the fundamentals at 2089.2 and 1960.2cm^{-1}. Thus, band b at 2077.0cm^{-1} is observed to appear at a much faster rate than band k at 1919.3cm^{-1}. It may therefore be proposed that from a purely qualitative standpoint, the CO groups *trans* to one another are more labile than the others. The $Mn(CO)_5X$ molecules are also expected to show different exchange rates for the axial and radial carbonyl groups, but when examined spectroscopically did not show this variation.[18,20] As discussed in Chapter II, this has most recently been explained by a fast intramolecular rearrangement taking place in the complexes.[21] The presence of the bulky phosphine ligand in *cis*-$Mn(CO)_4(PPh_3)Br$ may have hindered such a fast equilibration from taking place in this case. Quantitative kinetic studies on the isotopic exchange reactions of the *cis*-$Mn(CO)_4LX$ complexes would be highly valuable in this respect.

b. In $Mn(CO)_5Br$

The complexes *cis*-$Mn(CO)_4LBr$ ($L = SbPh_3$, $AsPh_3$) reacted with $C^{18}O$ to produce isotopically substituted $Mn(CO)_5Br$ as one of the two products. It was therefore felt that this reaction could be used to shed some light on the issue of intramolecular rearrangement in $Mn(CO)_5Br$. A substitution reaction of the type shown in equation 40, (assuming an S_N1 mechanism), would provide a product which has a $C^{18}O$ molecule specifically

$$cis\text{-}Mn(CO)_4LBr \xrightarrow{-L} Mn(CO)_4Br \xrightarrow{+C^{18}O} Mn(CO)_4(C^{18}O)Br \qquad (40)$$

in the radial position. Thus, the observation of any bands in the spectra which are attributable uniquely to the axially substituted species $Mn(CO)_4(C^{18}O)Br$ would have to be explained as arising from an intramolecular rearrangement of some sort.

Johnson *et al.*[20] observed that axial substitution produced a shift in the $\underline{a}_1$ (axial) mode to about 1958cm^{-1}. Unfortunately, the substrate spectra have fundamental absorptions near this frequency thus no direct experimental observation could be made. In view of this, the following experiments were performed.

1. The spectra in cyclohexane of the exchange mixture were recorded for *cis*-$Mn(CO)_4(SbPh_3)Br$ using a compensating solution of the substrate in the reference beam of the infrared spectrophotometer, in order to check whether any bands were superimposed with the substrate band at 1957.5cm^{-1}. The result was that a band did appear underneath the band at 1957.5cm^{-1} but was found to be at 1948.4cm^{-1} instead of the expected 1955-1960cm^{-1}. The band at 1948.4cm^{-1} was explained as arising from the shift in the vibration associated with the fundamental at 1957.5cm^{-1} when a CO in a position other than the one giving rise to it, is exchanged; (this was confirmed by the force constant calculations). This experiment would indicate, therefore, that no apparent rearrangement was taking place.

2. In order to eliminate the necessity of compensating for the substrate fundamentals, which is not a very reliable method of checking the superimposition of modes, given the difficulty of obtaining compensating solutions of the correct concentration, another experiment was performed. This consisted of stopping the exchange reaction at an early stage, removing the solvent in a stream of N_2, and subliming the bromopentacarbonylmanganese in a "mini" sublimer specially built for this purpose. The cold-finger of the sublimer was then washed with a very small

quantity of cyclohexane and the spectrum of the solution taken. Although the intensities of the resulting absorptions were weak (Figure 12) there was unmistakably a band around 1957cm^{-1}. The other bands observed were at 2069, 2051, 2019, and 1996cm^{-1}. These frequencies, due to the low intensities, are expected to be accurate only to ±2cm^{-1}. However, there is good evidence that both axially and radially substituted species of $Mn(CO)_4(C^{18}O)Br$ were present. It should be emphasized that when the reaction was stopped there was only a negligible amount of $Mn(CO)_3(C^{18}O)(SbPh_3)Br$ present.

3. Prior to concluding that an intramolecular rearrangement was actually taking place, it had to be demonstrated whether the substitution reaction proceeded via an S_N1 mechanism or not. For this reason the kinetics of the reaction of *cis*-$Mn(CO)_4(SbPh_3)Br$ with normal CO were investigated.

A stream of CO was bubbled through two *n*-hexane solutions of the substrate at different concentrations for the same period of time (2 min), which were then immediately thermostated at 35°C. Very low concentrations (0.31×10^{-3}M and 0.517×10^{-3}M) were used in order to ensure an excess of CO. The measured rates were 1.7×10^{-4}sec^{-1} and 1.5×10^{-4}sec^{-1}, respectively, and are believed to be accurate to ±15% considering the small concentrations used.

In conclusion, it may be stated that although the first experiment apparently indicates that no intramolecular rearrangement has taken place, the second, and more meaningful experiment indicates that such a rearrangement does indeed occur. Unfortunately, it is impossible to determine by the results of these experiments whether this intramolecular rearrangement

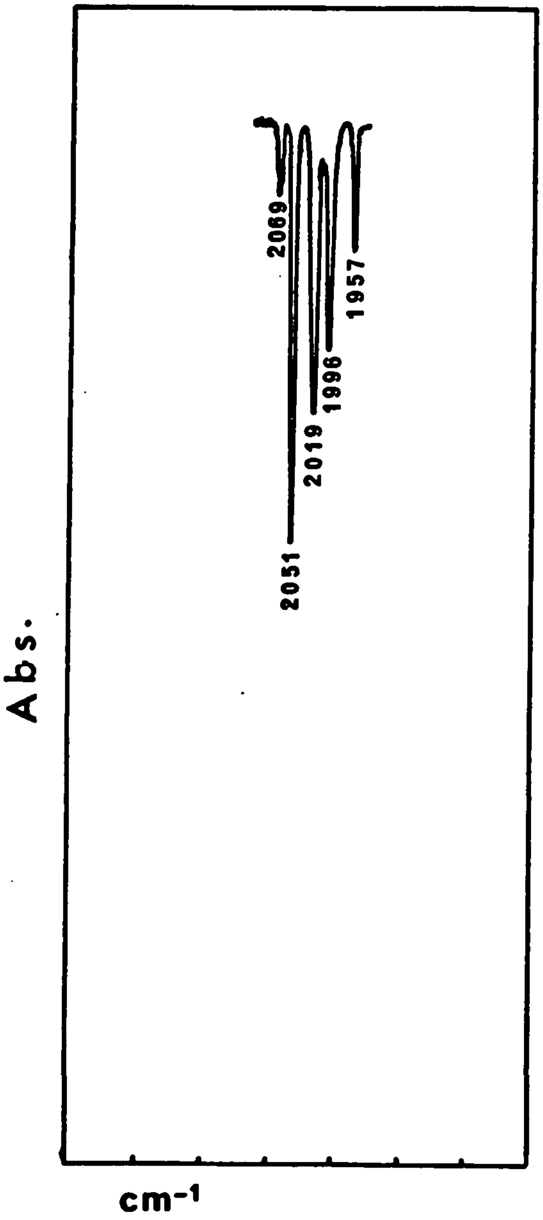

Figure 12.-Spectrum of $Mn(CO)_4(C^{18}O)Br$ in cyclohexane solution.

is taking place in the five-coordinate reactive intermediate, or in the bromopentacarbonylmanganese product. It would be worthwhile to repeat the above ligand substitution reaction with isotopic CO using a substrate free of bands in the 1965-1955cm^{-1} region. In this way, direct observation of the reaction product and an analysis of the relative intensities of the isotopic CO stretching frequencies could be made.

C. EXPERIMENTAL

The experimental technique used was identical in this study to that used in the previous one on the *cis*-$Fe(CO)_4X_2$ complexes. The substrates were prepared by the direct action of the appropriate ligands on $Mn(CO)_5Br$ and a subsequent work-up of the reaction mixtures following the general method outlined in the literature.[70]

APPENDIX

TABLE VIII. SUMMARY OF THE ISOTOPIC EXCHANGE STUDIES ON METAL CARBONYL COMPLEXES

COMPOUND	COMMENTS	NOTES	REF.
$Mo(CO)_6$	$C_8H_{10}Mo(CO)_3 + {}^{13}CO$, $C_7H_8Mo(CO)_4 + {}^{13}CO$	a,b	7
$Mo(CO)_6$	6-8% ^{13}CO-enrichment	a	2
$M(CO)_6$ (M = Cr, Mo, W)	$M({}^{13}C{}^{16}O)_6$, $M({}^{12}C{}^{18}O)_6$	a	8
$Cr(CO)_4$(*o*-phen)	stereospecific substitution, $C^{18}O$	b,c,d	9
$Re_2(CO)_{10}$	$HRe_3(CO)_{14} + {}^{13}CO$, stereospecific substitution	a,b	13
$Mn_2(CO)_{10}$	Irradiation, ^{13}CO	a	14
$M(CO)_5X$ (M = Mn,Re; X = Cl,Br,I)	^{13}CO	a,b	18
$Mn(CO)_5X$ (X = Cl,Br)	$C^{18}O$	a,b,d,f	19,20
$M(CO)_5Y$ (M = Mn,Re; Y = H,D)	^{13}CO	a,b	23
$CH_3Mn(CO)_5$	$CH_3{}^{13}COMn(CO)_5 \rightarrow \textit{cis}\text{-}CH_3Mn(CO)_4{}^{13}CO + CO$	a,b,d	25,27
$CH_3Mn(CO)_5$	$\textit{cis}\text{-}CH_3COMn(CO)_4{}^{13}CO \rightarrow \textit{cis/trans}\text{-}CH_3Mn(CO)_4{}^{13}CO + CO$	a,b,d	25,27
$CH_3COMn(CO)_5$	$CH_3Mn(CO)_5 + {}^{13}CO \rightarrow \textit{cis}\text{-}CH_3COMn(CO)_4{}^{13}CO$	a,b,d	25,27
$CH_3COMn(CO)_5$	$NaMn(CO)_5 + CH_3{}^{13}COCl \rightarrow CH_3{}^{13}COMn(CO)_5$	a,b,d	25,27
$CH_3COMn(CO)_5$	$\textit{cis}\text{-}CH_3Mn(CO)_4{}^{13}CO + CO \rightarrow \textit{cis/trans}\text{-}CH_3COMn(CO)_5 + CH_3{}^{13}COMn(CO)_5$	a,b,d	25,27
$X_3M'Mn(CO)_5$ (X = Ph,Br; M = Ge,Sn)	axial, radial relative force constant value reversal, ^{13}CO	a	30
$Fe(CO)_5$	sunlight, ^{13}CO	a	31

$Fe(CO)_5$	$Fe + C^{18}O$, $Fe(CO)_5 + {}^{13}CO(C^{18}O)$ by u.v. light, supported Pd, CF_3COOH	b,c,d	34
$Ni(CO)_4$	$Ni(CO)_{4-n}(C^{18}O)_n$, vapour and liquid	c,d	37,38
$Ni(CO)_4$	$Ni + C^{18}O$	a	39
$Ni(CO)_4$	${}^{13}CO$, 22% enrichment	a	40
$Ni(CO)_4$	$Ni({}^{12}C^{18}O)_4$, $Ni({}^{13}C^{16}O)_4$	a	41
$Co_2(CO)_8$	${}^{13}CO$	e	42
$Co(CO)_3NO$	${}^{13}CO$, ${}^{15}NO$	a	44
$Co(CO)_3NO$	${}^{13}CO$, 22% enrichment	a	40
$Hg[Co(CO)_4]_2$	$Hg + Co_2(CO)_7{}^{13}CO$	a	42
$Co(CO)_3(PPh_3)(COCH_2Ph)$	$Co(CO)_3(PPh_3)(CH_2Ph) + {}^{13}CO\ Co(CO)_2({}^{13}CO)(PPh_3)(COCH_2Ph)$	b,d	46
cis-$Fe(CO)_4I_2$	$C^{18}O$	a,b,f	47
cis-$Fe(CO)_4X_2$ (X = Br,I)	${}^{13}CO$	a,b	62
$C_4H_6Fe(CO)_3$	${}^{13}CO$	a,b	70
$Rh_2(CO)_4X_2$ (X = Cl,Br,I,SEt,SPh)	$C^{18}O$	a	48

a : infrared spectra and force constant calculations.

b : exchange stereochemistry.

c : kinetics.

d : mechanistic studies.

e : to be published.

f : intensity studies.

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PART III

REACTIONS OF BROMOPENTACARBONYLMANGANESE(I) AND ITS DERIVATIVES WITH PHOSPHITES AND CHELATING LIGANDS

CHAPTER I INTRODUCTION

Extensive studies of the reactions of halopentacarbonylmanganese and rhenium complexes with a host of ligands have been carried out, initiated mainly by Hieber and his co-workers (see refs. in Table I). The results of these investigations may be summarized by the following reaction sequence

$$M(CO)_5X + L \longrightarrow M(CO)_4LX \longrightarrow M(CO)_3L_2X$$

Table I lists examples of the substituted halotetracarbonyl and halotricarbonyl complexes of manganese and rhenium isolated or spectroscopically identified to date. That no further substitution of the carbonyl groups in the tricarbonyl complexes has been observed has not been fully explained. However, a consideration of the bonding of these complexes indicates that the replacement of CO by a ligand which is not as good a π-electron acceptor as itself, will lead to a strengthening of the remaining metal-CO bonds. This is because there would be a greater electron density on the central metal atom in the substituted species available for back-bonding to the remaining carbonyl groups with consequent strengthening of the metal-carbon bonds. This has been verified experimentally, for example, by Bigorgne,[21] who calculated the nickel-carbon stretching force constants for a series of complexes $Ni(CO)_{4-n}L_n$ and found that they increased with increasing substitution of CO, and also that the more basic ligands served to strengthen the Ni-C bonds most.

In 1963, Joshi, Pauson, and Stubbs[17] investigated the reaction of phenyl isocyanide (PhNC, a ligand which is similar to CO in its mode of

TABLE I. COMPOUNDS OF GENERAL FORMULA $M(CO)_4LX$ AND $M(CO)_3L_2X$

(M = Mn, Re; X = Cl, Br, I) ISOLATED OR IDENTIFIED TO DATE

M	X	L in $M(CO)_4LX$	L in $M(CO)_3L_2X$
Mn	Cl	PPh_3,[1,3] $AsPh_3$,[1] $TePh_2$,[2] 3-Cl-py,[4]	PPh_3,[5,7] $AsPh_3$,[5,7] $SbPh_3$,[5,6] dipy,[5] py,[5] an,[5] *o*-phen,[5,6] $TePh_2$,[2,6] $TePh_2$,[2,6] $TeOC_{12}H_8$,[2]
	Br	PPh_3,[1,3,9] $AsPh_3$,[1,9] $SbPh_3$,[1,9] $PPhCl_2$,[1,9] $P(OCH_2)_3$ CCH_3,[1,3] $P(OPh)_3$,[1,9] $P(OBu)_3$[1,9] PPh_2Cl,[9] 3-Cl-py,[4] CNPh,[17] C_2H_5NC,[1]	PPh_2Cl,[1,9] $P(OCH_2)CCH_3$,[1,9] $P(OPh)_3$,[1,8,9] $P(OBu)_3$,[1,8,9] *o*,*p*-$CH_3C_6H_4NH_2$,[1] $C_6H_5NH_2$,[1] PPh_3,[7] $AsPh_3$,[7] $PPhCl_2$,[8,9] PBu_3,[8] dithia,[10] 3,6,9,-trithiaundecane,[10] $TePh_2$,[2,6] py,[5] *o*-phen,[5] diphos,[11] diars,[11] disulph,[11] CNPh,[17] C_2H_5NC,[1] *p*-CNC_6H_4OMe,[5]
	I	PPh_3,[1,3] $AsPh_3$,[1] py,[4] 3-Cl-py,[4] 4-CH_3-py,[4]	PBu_3,[1] $TePh_2$,[2,6] py,[4,7] dipy,[7] PPh_3,[7] $AsPh_3$,[7] diphos,[11] diars,[11] disulph,[11] *o*-phen,[5,6] dien,[12]
Re	Cl	NH_3,[13] PPh_3,[18] py,[18] γ-pic,[18]	py,[5,7,14] *o*-phen,[5] $C_6H_5NH_2$,[13] PPh_3,[7,14,19] $AsPh_3$,[7] dipy,[14] CNR,[13] PPh_2Me,[19] PPh_2H,[19] diphos,[19] PBu_3,[19] $P(OMe)_3$,[19] Tdp,[19] TMED,[19] $C_5H_{11}N$,[19] [PPh_3.py],[15]
	Br	PPh_2Et,[15] PBu_3,[15] PPh_3,[18] py,[18] γ-pic,[18]	py,[5] *o*-phen,[5] dipy,[14] PPh_3,[15] γ-pic,[15] PPh_2Et,[15] [PPh_2Et.py],[15] [PBu_3.PPh_3],[15]
	I	PPh_3,[18,20] py,[18] γ-pic,[18]	py,[5,7,14,15,16] *o*-phen,[5,16] dipy,[7,14] PPh_3,[7,20] $AsPh_3$,[7]

bonding to a transition metal) with halocarbonylmanganese complexes, and found that under the appropriate experimental conditions, a whole range of $Mn(CO)_{5-n}L_nX$ (n = 1-5 for X = Br; n = 1-4 for X = I) complexes could be isolated. For X = Cl, the reaction proceeded even further than the elimination of all the CO groups, with the formation of $(MnL_6)Cl$. Miles and Clark[22] have reported that $Mn(CO)_5H$ reacts with PF_3 under ultraviolet light to yield species of all the possible compositions $Mn(CO)_{5-n}(PF_3)_nH$. Both PhNC and PF_3 are better π-electron acceptors than CO, thus the strengthening of the remaining M-CO bonds on substitution, discussed above, does not take place. Abel and Tyfield[19] have recently identified compounds of the type *cis*-$Re(CO)_2L_3Cl$[L = PPh_2H, PPh_2Me, $P(OPh)_3$]; and similar iododicarbonylrhenium complexes are also known.[20]

Non-halodicarbonyls of the Group VIIB metals, other than the hydrides, are also known. The most commonly encountered are dicarbonyl complexes containing the cyclopentadienyl ion (or one of its derivatives) as one of the ligands attached to the central metal atom, and of the general formula $M(CO)_2(C_5H_5)L$.[23,24] Booth *et al.*[25] have found that reaction of $PhMn(CO)_5$ with an excess of $P(OCH_2)_3CEt$ in the absence of solvent at 100° gives, in part, *trans*-$PhCOMn(CO)_2L_3$. An interesting ionic dicarbonyl is $[Mn(CO)_2dipy(PPh_3)_2]NO_3$ which was prepared by the reaction of $Mn(CO)_3$-(dipy)NO_3 with PPh_3.[26] Recently, Moelwyn-Hughes and Garner[27] have prepared a nitrogen complex of Re(0): $Re(CO)_2(NH_2)N_2L_2$ (L = PMe_2Ph) from the reaction of hydrazine with *trans*-$Re(CO)_3L_2Cl$.

However, apart from $Mn(CO)_2(PhNC)_3X$,[17] there do not appear to be any other reports of halodicarbonylmanganese complexes in the literature.

There exists some evidence which indicates that the substitution process may be arrested at the tricarbonyl stage because of the inability of the central metal atom to accommodate any more bulky ligands in its coordination sphere. Thus, for example, the *cis*-$Mn(CO)_3L_2Br$[L = $P(OPh)_3$, *n*-$P(OBu)_3$, *n*-PBu_3, $PPhCl_2$] complexes are known to isomerize to the *trans*-derivatives,[8] in which the tertiary phosphine ligands are less crowded. The fact that the formation of only *cis* complexes (except for L = PPh_3) was observed in similar complexes containing the larger and therefore presumably more accommodating rhenium atom,[19] also supports this thesis.

In view of the above, it was decided to study the reactions of the halopentacarbonyls, $Mn(CO)_5X$, with smaller (*i.e.* less bulky) ligands than had heretofore been used. It was found that even under the relatively mild conditions of refluxing chloroform, three carbonyl groups were easily replaced by phosphites such as $P(OMe)_3$, with the formation of *cis*-$Mn(CO)_2L_3X$. When these complexes were reacted with the bidentate ligand diphos ($PhP_2CH_2CH_2PPh_2$), two of the L groups were replaced with the resulting formation of mixed ligand complexes of the type *cis*-$Mn(CO)_2L$(diphos)X. Furthermore, when the bidentate ligands: diphos, diarsine ($Ph_2AsCH_2CH_2AsPh_2$), diars (*o*-Ph[$As(CH_3)_2$]), and dipy, were reacted with *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$, two products were obtained, *cis*-$Mn(CO)_2[P(OPh)_3]$(bidentate)Br, and *cis*-$Mn(CO)_3$(bidentate)Br.

The potentially tridentate ligand triphos, $PhP(CH_2CH_2PPh_2)_2$, reacted with $Mn(CO)_5Br$ to give *cis*-$Mn(CO)_3$(triphos)Br in which the ligand is functioning as a bidentate ligand. The third and uncoordinated phosphorus was found to replace a CO group on another $Mn(CO)_5Br$ molecule to give an apparently phosphine bridged species, $BrMn(CO)_3$(triphos)$Mn(CO)_4Br$.

CHAPTER II RESULTS AND DISCUSSION

A. PREPARATION OF THE COMPLEXES

The *cis*-$Mn(CO)_2L_3X$ complexes [L = $P(OMe)_3$, $P(OEt)_3$, and $P(OCH{:}CHCH_3)_3$, for X = Br; and L = $P(OMe)_3$ for X = Cl] were all prepared by refluxing the halopentacarbonylmanganese complex with slightly over a three-fold excess of the appropriate ligand for varying periods of time. In every case the reactions had proceeded to the tricarbonyl stage after one hour, as evidenced from changes in the i.r. spectra of the reaction mixtures. Slower reactions then transformed the tricarbonyl complexes to the dicarbonyl ones. A qualitative comparison of the rates of formation of the chloro- and bromo- complexes, *cis*-$Mn(CO)_2[P(OMe)_3]_3X$ indicated that, as expected,[1,2] the former was formed much faster than the latter.

Although it was hoped that similar reactions in diglyme and THF would lead to further substitution as was the case with the ligand PhNC[17] (these solvents act as multidentate ligands stabilizing the intermediates formed), this was not observed. Thus, reaction of $Mn(CO)_5Br$ with $P(OPh)_3$ in diglyme at 100° resulted in complete decomposition, while reaction of *cis*-$Mn(CO)_2[P(OMe)_3]_3X$ (X = Cl, Br) with excess $P(OMe)_3$ in THF gave no new product.

The *cis*-$Mn(CO)_2[P(OMe)_3]_3X$ complexes reacted in refluxing chloroform with diphos to give *cis*-$Mn(CO)_2[P(OMe)_3](diphos)X$. The complexes crystallized with $CHCl_3$ in their lattices: one molecule for the bromide, and half a molecule for the chloride. Such solvation behaviour has been noted previously for complexes of the type $M(CO)_2(diphos)_2X_2$ (M = Mo, W; X = Cl, Br) which showed a great tendency to crystallize as dichloroethane adducts.[28] When a chloroform solution of *cis*-$Mn(CO)_2[P(OMe)_3]_3Br$ and dipy was refluxed, no change in the i.r. spectrum of the reaction mixture was observed even after 54hr.

In terms of mechanism the reactions of *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$ with the bidentate ligands diphos, diarsine, diars and dipy are particularly interesting. The general procedure was to reflux a mixture of the substrate, the bidentate, and $P(OPh)_3$ in chloroform for a certain period of time, the latter being determined by monitoring the disappearance of the i.r. bands of the substrate. In all cases, it was found that two products were obtained, one of which was *cis*-$Mn(CO)_3$(bidentate)Br, the other *cis*-$Mn(CO)_2L$(bidentate)Br. The two products could be separated by chromatography on an alumina column using benzene: petroleum ether mixtures as eluents. (The product of the dipy reaction was developed using a benzene: chloroform mixture and eluted with ethanol.) However, the separation of the two products on the column was never quite complete and the correct fractions had to be taken for analytical purposes.

In these reactions the excess $P(OPh)_3$ was added because this was found to decrease the proportion of the undesired tricarbonyl formed. (However, the formation of the latter could never be completely eliminated in this way.) No change in the time taken for the formation of the dicarbonyl was noted. The infrared spectra of the reaction product of *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$ and diphos when excess $P(OPh)_3$ was, and was not used, are contrasted in Figure 1.

The fact that two ligands were being replaced by the chelating ligand suggests that the dicarbonyl was produced by either first replacing the CO with one end of the chelating ligand, which on closing displaced the

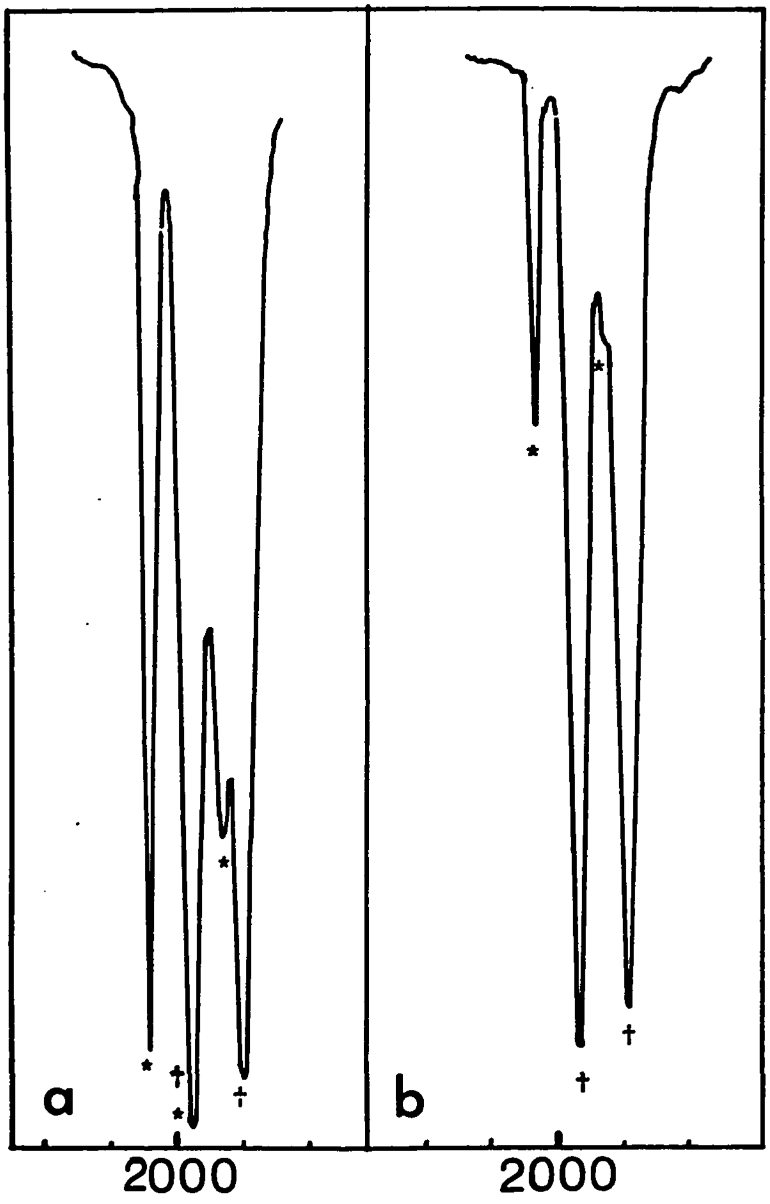

Figure 1.-Infrared spectra in the CO stretching region (in chloroform) of the products of the reaction between *trans*-Mn$(CO)_3[P(OPh)_3]_2$Br and diphos, showing the effect of addition of excess $P(OPh)_3$ on the distribution of the products; (a) without added $P(OPh)_3$ (b) with added $P(OPh)_3$. The bands marked * are due to *cis*-Mn$(CO)_3$(diphos)Br, while those marked † are due to *cis*-Mn$(CO)_2[P(OPh)_3]$(diphos)Br.

$P(OPh)_3$ or *vice versa*. The tricarbonyl must have been produced by a sequential (or simultaneous) elimination of the two $P(OPh)_3$ groups. Therefore assuming an S_N1 mechanism, any added $P(OPh)_3$ would retard the initial slow replacement of the first coordinated $P(OPh)_3$ and thus decrease the proportion of tricarbonyl formed. That no appreciable change in the rate of production of dicarbonyl occurred would tend to indicate that the latter was mainly produced by a mechanism in which a CO group was first replaced, followed by a fast ring-closing step in which a $P(OPh)_3$ molecule is eliminated. This is shown schematically in Figure 2.

When the reaction of *trans*-$Mn(CO)_3(PPh_3)_2Br$ with diphos was attempted, the changes in the i.r. spectrum of the reaction mixture indicated the formation of a very small proportion of the dicarbonyl complex, with the majority of the product being *cis*-$Mn(CO)_3$(diphos)Br. The small quantity of *cis*-$Mn(CO)_2(PPh_3)$(diphos)Br formed had disappeared by the time all of the substrate had reacted. This may indicate that the size of the outgoing ligand, in this case the bulky PPh_3, plays an important role in the ratio of the two products formed in these reactions.

In the event that in the reaction with $P(OPh)_3$ the *cis*-$Mn(CO)_3$(diphos)Br formed was produced by the thermal decomposition of *cis*-$Mn(CO)_2[P(OPh)_3]$(diphos)Br, the latter was isolated and refluxed in chloroform. After ten hours, an unidentified reaction seemed to be taking place, but was too slow for the above statement to be true. The thermal decomposition reaction was not investigated further.

When *cis*-$Mn(CO)_3[P(OPh)_3]_2Br$ was reacted with diphos, the proportion of tricarbonyl produced was very much greater than when the *trans*-isomer was used. This may indicate that a higher activation energy

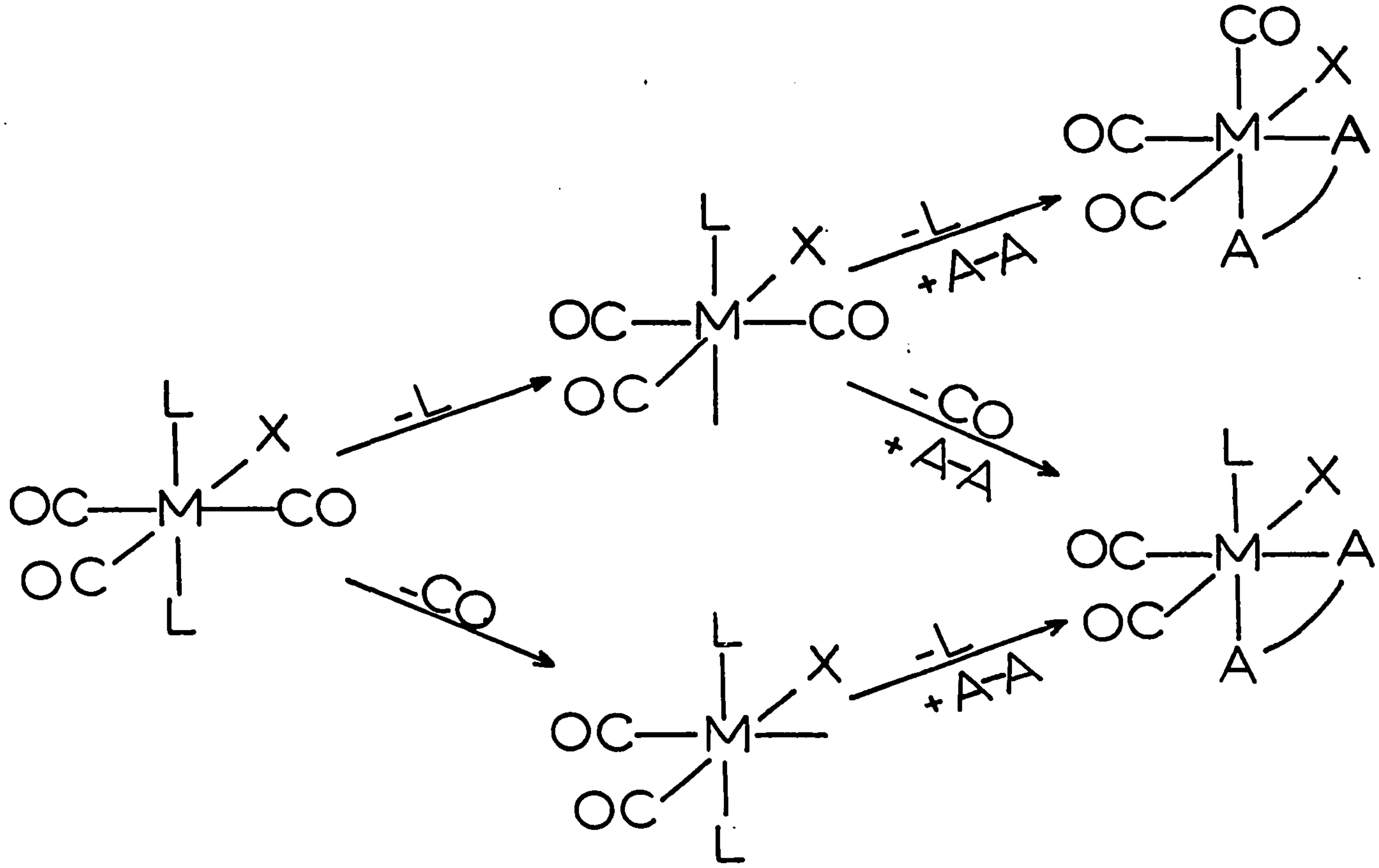

Figure 2.-Possible pathways in the reaction of *trans*-Mn(CO)$_3$L$_2$X with bidentates (A-A).

is necessary to rearrange the latter complex in the formation of *cis*-Mn$(CO)_3$(bidentate)Br, but may also be due to the greater relief in steric crowding secured on going to the tricarbonyl from the *cis*-complex. Similarly in the substitution of the ligands L in *cis*-/*trans*-Mo$(CO)_4L_2$ by dipy the reactions have been found[29] to proceed at a faster rate with the *cis* complexes than with the *trans* species. These observations corroborate the results of the reaction between *trans*-Mn$(CO)_3(PPh_3)_2$Br and diphos described above.

It has been noted previously[30] that dipy is a labilizing ligand in the system Mo$(CO)_4$(dipy), CO replacement being easier in this complex than in Mo$(CO)_6$. It was therefore hoped that *cis*-Mn$(CO)_2[P(OPh)_3]$(dipy)Br could be prepared by the reaction of *cis*-Mn$(CO)_3$(dipy)Br with $P(OPh)_3$, but all such attempts proved fruitless and only resulted in decomposition. Also, it was thought that *cis*-Mn$(CO)_4[P(OPh)_3]$Br might react with bidentates replacing two CO groups, but this was not found to be the case and *cis*-Mn$(CO)_3$(bidentate)Br was the sole product formed.

A preliminary investigation on the reactions of the potentially tridentate ligand triphos, $PhP(CH_2CH_2PPh_2)_2$, with a number of halocarbonylmanganese complexes has been carried out. The reaction of triphos with Mn$(CO)_5$X(X = Cl, Br) afforded complexes with the general formula *cis*-Mn$(CO)_3$(triphos)X in which the ligand acted as a bidentate. The presence of three carbonyl groups in these complexes is supported by the infrared carbonyl stretching vibrations. The three bands observed appear in much the same pattern and at very similar frequencies to those of *cis*-Mn$(CO)_3$(diphos)Br. Chiswell and Venanzi[31] have reported that the quadridentate ligand tris-(*o*-diphenylphosphinophenyl)phosphine,(QP), when refluxed in diglyme with $Mn(CO)_5X$(X = Cl, Br) coordinated as a bidentate to give *cis*-$Mn(CO)_3(QP)X$.

Continued refluxing of the reaction products, *cis*-$Mn(CO)_3$(triphos)X, in chloroform indicated that a further, but very slow, reaction was taking place. A new band appeared in the region where the lower of the two CO stretching frequencies of the dicarbonyl would be expected to occur. Even after 150 and 60hr in the case of the bromide and chloride, respectively, the reactions were still far from complete. The nature of these further reactions is open to conjecture, but it probably involves the attachment of the third phosphorous to the manganese atom. It is also not clear at the present time which of the three phosphorous atoms remains unattached in *cis*-$Mn(CO)_3$(triphos)Br.

The uncoordinated phosphorous in the bromo-complex was found to easily eliminate a CO group from another $Mn(CO)_5Br$ molecule to form, presumably, a phosphine bridged complex, $BrMn(CO)_3$(triphos)$Mn(CO)_4Br$. The compound was identified by its infrared spectrum which was almost identical to a superimposition of those of *cis*-$Mn(CO)_4(PPh_3)Br$ and *cis*-$Mn(CO)_3$(triphos)Br. One possible structure for this bridged species is shown in Figure 3. The infrared spectra of a sequence of samples taken

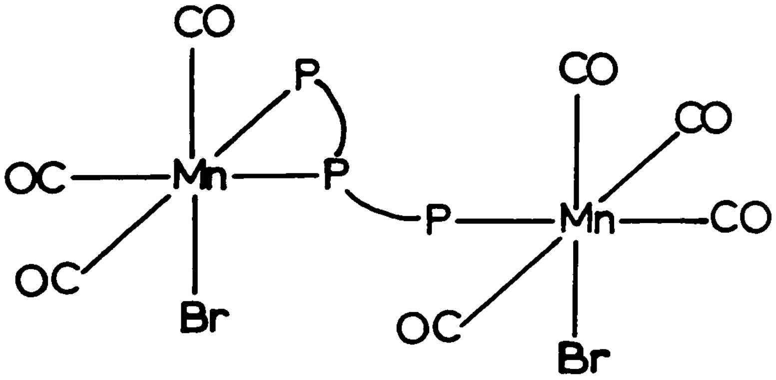

Figure 3.-Possible structure of the reaction product of $Mn(CO)_5Br$ with *cis*-$Mn(CO)_3$(triphos)Br. (The Ph and CH_2 groups have been omitted for the sake of clarity.)

from the reaction mixture are shown in Figure 4. The compound with the bridging triphos appeared not to be very stable in solution and to revert easily to *cis*-$Mn(CO)_3$(triphos)Br. This was concluded from noticing that when *n*-hexane was added to a chloroform solution of $BrMn(CO)_3$(triphos)-$Mn(CO)_4Br$, the infrared spectrum of the precipitated complex in chloroform contained a much larger proportion of *cis*-$Mn(CO)_3$(triphos)Br than the original chloroform solution did.

It would seem, however, that triphos, as well as the other tri- and terdentate ligands used by Chiswell and Venanzi[31] could be very useful in preparing a host of bridging complexes containing the same metal, two different metals, etc. This would be well worth examining further.

The ligand triphos was also refluxed with *cis*-$Mn(CO)_2[P(OMe)_3]_3Cl$ and the reaction monitored in the carbonyl stretching region. The two symmetric bands of the substrate began to broaden and assymmetrize, but after 2.5hr they were once again symmetric though shifted from 1979 and $1892cm^{-1}$ to 1950 and $1872cm^{-1}$. Refluxing for a further twelve hours produced no change. Barring the formation of ionic species, the infrared spectrum would indicate the formation of either *cis*-$Mn(CO)_2$(triphos)Cl or *cis*-$Mn(CO)_2[P(OMe)_3]$(triphos)Cl, where triphos acts as a tridentate or a bidentate ligand, respectively. The proximity of the CO stretching frequencies to those of *cis*-$Mn(CO)_2[P(OMe)_3]$(diphos)Cl perhaps favours the latter, as would the account given above on the reaction of triphos with $Mn(CO)_5X$.

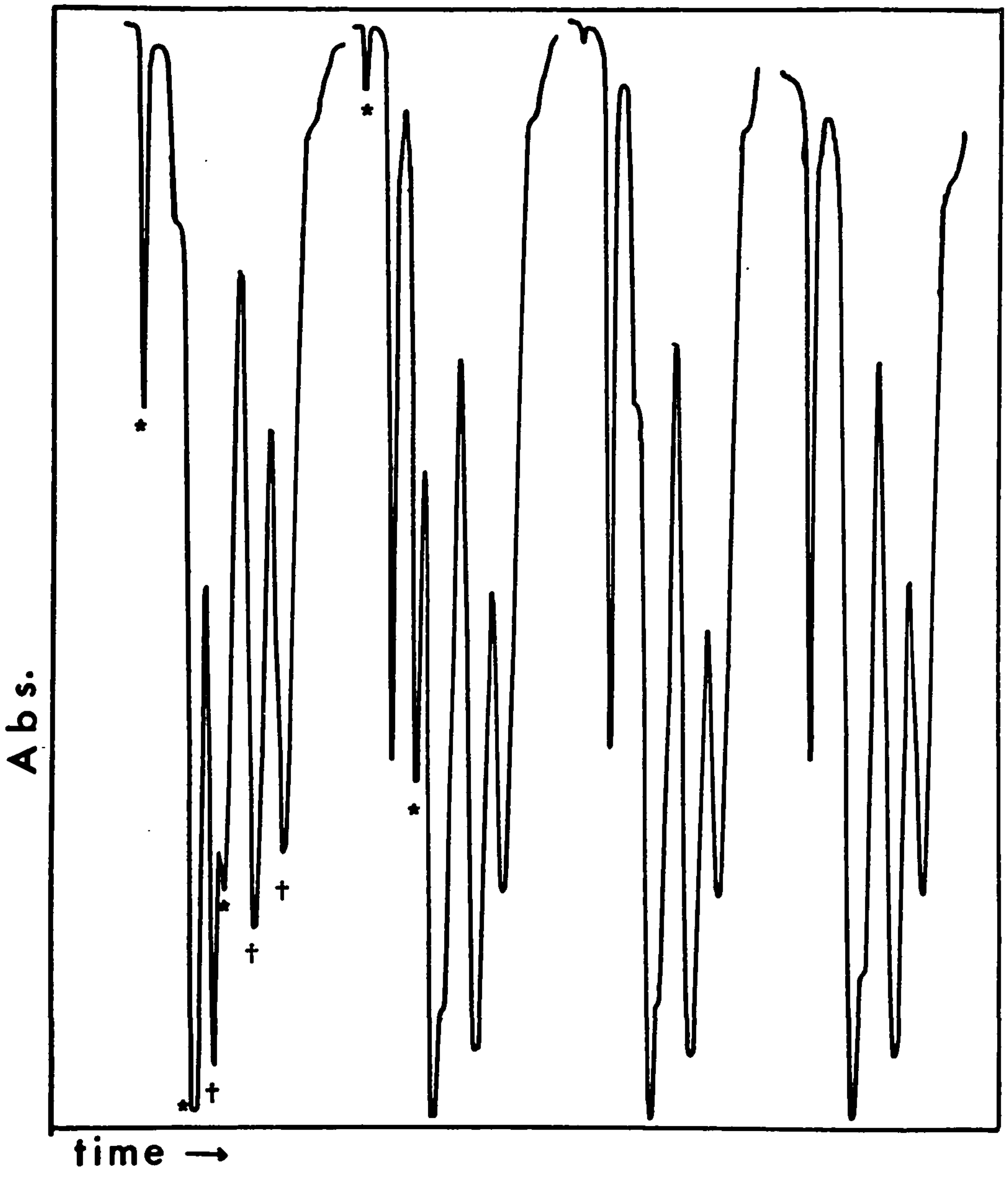

Figure 4.-Sample spectra recorded from the reaction mixture of $Mn(CO)_5Br$ and *cis*-$Mn(CO)_3$(triphos)Br in chloroform. The bands marked * are due to $Mn(CO)_5Br$, while those marked † are due to *cis*-$Mn(CO)_3$(triphos)Br.

B. INFRARED SPECTRA AND STRUCTURES OF THE COMPLEXES

The infrared spectra in the carbonyl stretching region of chloroform solutions of the complexes identified are given in Table II. The dicarbonyls all exhibit three strong bands, consistent with an all *cis*-structure, while all the dicarbonyls exhibit two equally intense bands. The spectra of the latter indicate that the two CO groups are in mutually *cis* positions. If they were in *trans* positions, only one strong band (antisymmetric stretch) would be expected for the $Mn(CO)_2L_3X$ molecules; and one very weak band (symmetric stretch) and one strong band (antisymmetric stretch) for the $Mn(CO)_2L(A\text{-}A)X$ molecules. Sample spectra are shown in Figure 5.

For the compounds, $Mn(CO)_2L_3X$ the structures I, II, or III shown in Figure 6 are possible, while for the $Mn(CO)_2L(A\text{-}A)X$ complexes the choice of structures would lie among IV, V, VI, or VII shown in Figure 6. Structures I and VII can be immediately eliminated because of the arguments presented above on the infrared spectra. It is impossible at present to differentiate between structures II and III, but the fact that the CO *trans* to the halogen is expected to be the least labile[6,32] and therefore the least liable to substitution would make structure II the more likely one. This argument alone would point to structure VI as the most likely one for the other complexes. However, a consideration of the proposed structure of the *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$[8] from which some of the complexes of this type were obtained would also indicate that, barring any seemingly unnecessary rearrangement, and remembering that there are no *trans*-CO groups present in the bidentate containing complexes, structure VI would be the only structure possible.

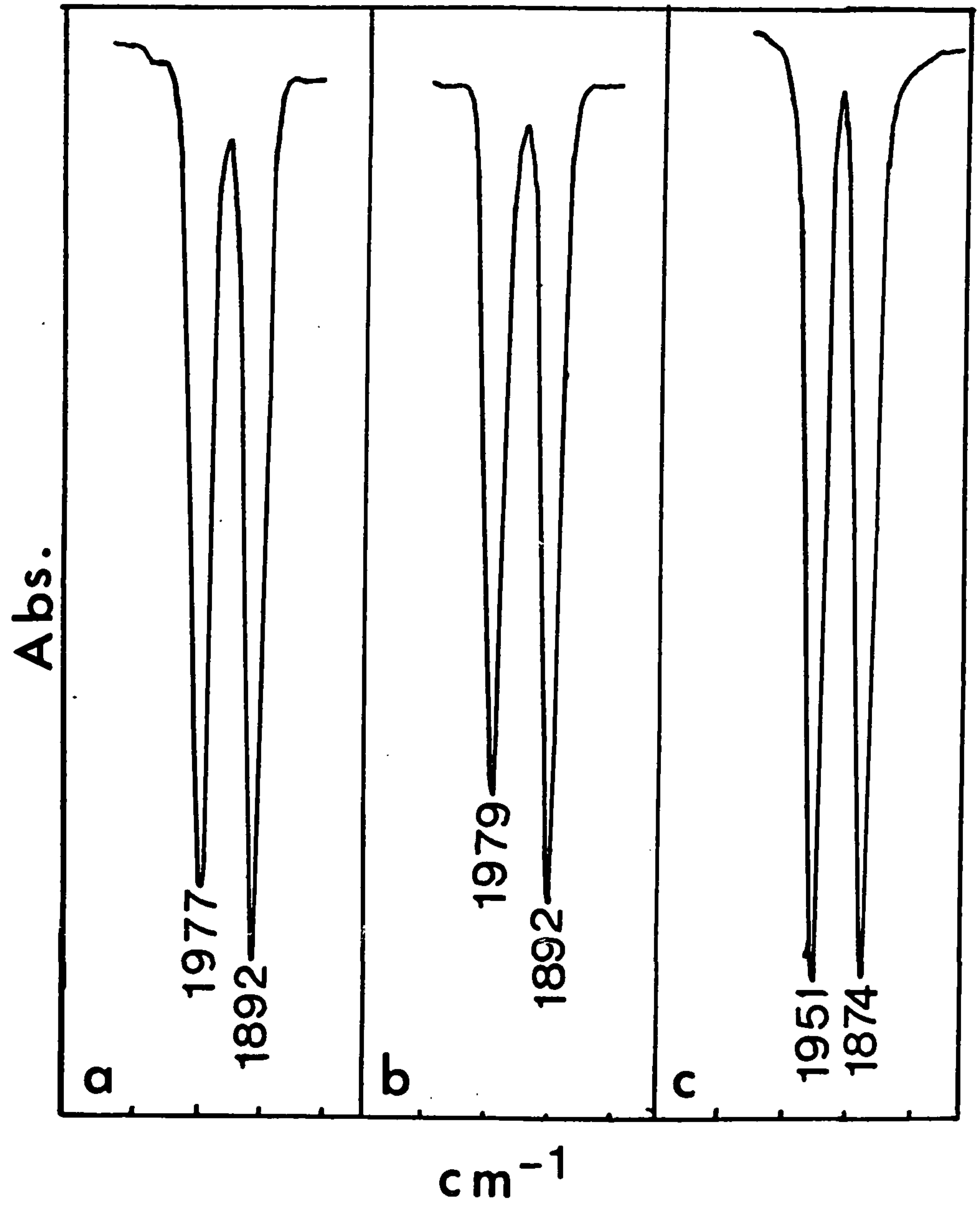

Figure 5.-Infrared spectra in the CO stretching region in chloroform of (a) *cis*-Mn(CO)$_2$[P(OMe)$_3$]$_3$Br (b) *cis*-Mn(CO)$_2$[P(OMe)$_3$]$_3$Cl (c) *cis*-Mn(CO)$_2$[P(OMe)$_3$](diphos)Cl.

TABLE II. INFRARED SPECTRA IN THE CO STRETCHING REGION OF SOME MANGANESE CARBONYL COMPLEXES IN CHLOROFORM (cm^{-1})

Compound	ν(CO)[a]
cis-Mn(CO)$_3$(diphos)Br	2025, 1959, 1919
cis-Mn(CO)$_3$(triphos)Cl	2027, 1958, 1914
cis-Mn(CO)$_3$(triphos)Br	2025, 1959, 1915
cis-Mn(CO)$_3$(diarsine)Br	2026, 1957, 1919
cis-Mn(CO)$_3$(dipy)Br	2033, 1945, 1924
cis-Mn(CO)$_2$[P(OMe)$_3$]$_3$Cl	1979, 1892
cis-Mn(CO)$_2$[P(OMe)$_3$]$_3$Br	1977, 1892
cis-Mn(CO)$_2$[P(OEt)$_3$]$_3$Br	1971, 1877
cis-Mn(CO)$_2$[P(OCH:CHCH$_3$)$_3$]$_3$Br	1977, 1894
cis-Mn(CO)$_2$[P(OMe)$_3$](diphos)Cl	1951, 1874
cis-Mn(CO)$_2$[P(OMe)$_3$](diphos)Br	1950, 1876
cis-Mn(CO)$_2$[P(OMe)$_3$](triphos)Cl	1950, 1872
cis-Mn(CO)$_2$[P(OCH:CHCH$_3$)$_3$](diphos)Br	1951, 1877
cis-Mn(CO)$_2$[P(OPh)$_3$](diphos)Cl	1962, 1883
cis-Mn(CO)$_2$[P(OPh)$_3$](diphos)Br	1962, 1833
cis-Mn(CO)$_2$[P(OPh)$_3$](diarsine)Br	1960, 1886
cis-Mn(CO)$_2$[P(OPh)$_3$](dipy)Br	1981, 1913
cis-Mn(CO)$_2$[P(OPh)$_3$](diars)Br	1960, 1880
BrMn(CO)$_3$(triphos)Mn(CO)$_4$Br	2093, 2026, 2011(sh), 1960, 1917

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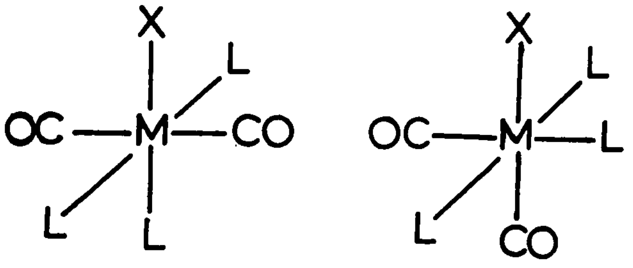
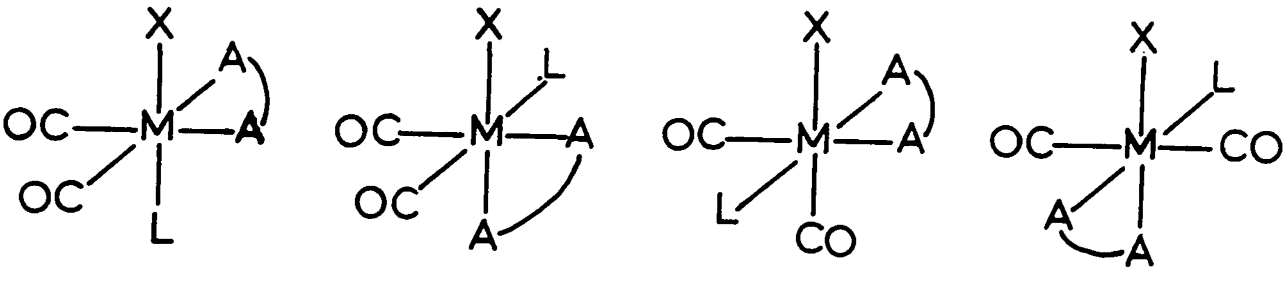
[a] All the bands are strong, the frequencies are accurate to ± 1cm^{-1}.

The infrared spectra of the bidentate ligand containing complexes cannot, in themselves, or along with the elemental analyses, discount the possibility of them being bidentate bridged. Examples of such bridging are known for molybdenum[33] and halomolybdenum[34] carbonyls. However, a molecular weight determination for *cis*-$Mn(CO)_2[P(OPh)_3](diphos)Br$ indicated that this complex is monomeric, and so presumably are the other bidentate containing dicarbonyls.



(I) (II) (III)

Figure 6.-Various structures for the complexes $Mn(CO)_2L_3X$.



IV V VI VII

Figure 7.-Various structures for the complexes $Mn(CO)_2L(A-A)X$.

CHAPTER III EXPERIMENTAL

A. STARTING MATERIALS AND MEASUREMENTS

The primary materials, $Mn_2(CO)_{10}$, various ligands, and solvents were obtained from the sources given in the table on p.iii. The $Mn(CO)_5X$ (X = Cl, Br) compounds were prepared by the method of Abel and Wilkinson.[7] The substituted compounds *cis/trans*-$Mn(CO)_3[P(OPh)_3]_2X$ and *trans*-$Mn(CO)_3$-$(PPh_3)_2Br$, were prepared by the general methods described by Basolo and his co-workers.[1,8,9]

The infrared spectra were recorded using 1.00mm NaCl solution cells on a Perkin Elmer model 337 spectrophotometer coupled to a Texas Instruments Servo/riter model II recorder. Calibrations were performed using a 10cm carbon monoxide filled gas cell ($2143.2cm^{-1}$) and polystyrene ($1583.1cm^{-1}$).

The n.m.r. and mass spectra were recorded on a Varian model A-60 (in $CDCl_3$) and an AEI model MS902, respectively.

The melting point measurements were made on a Gallenkamp Melting Point Apparatus, using sealed capillary tubes and are uncorrected.

The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York. The molecular weight determination of *cis*-$Mn(CO)_2[P(OPh)_3](diphos)Br$ was carried out by Mikroanalytisches Laboratorium Beller, Göttingen, Germany, using the method of vapour pressure osmometry.

B. PREPARATION OF COMPLEXES

Not all of the complexes whose preparations are described below were sent for elemental analysis. In these cases the i.r. spectra were taken as sufficient proof of identity.

All the complexes were found to be very soluble in polar solvents.

Bromodicarbonyltris(trimethylphosphite)manganese(I):-

A mixture of $Mn(CO)_5Br$(0.98g) and $P(OMe)_3$(1.60g) in 60ml of chloroform was refluxed for 25hr after which time the solvent was reduced to 5ml on a rotary evaporator, and 50ml of *n*-hexane added. This mixture was again reduced to 5ml and the solid precipitate filtered off. The procedure was repeated with the filtrate until most of the desired product remained on the filter. The solid product was then dissolved in 2ml of chloroform and recrystallized in the form of orange needles from *n*-hexane at 0°. (Yield: 1.45g, 72%; mp: 143-145°) *Anal.* Calcd for $C_{11}H_{27}O_{11}P_3MnBr$: C, 23.46; H, 4.83; P, 16.50; Br, 14.19. Found: C, 23.56; H, 4.52; P, 14.56; Br, 15.45. *Mol.wt.* (mass spectrum) Calcd: 563. Found: 563. In the ^1H n.m.r. spectrum a multiplet centered at $\tau = 6.18$p.p.m. was observed, caused by phosphorous-proton(CH_3) coupling. In addition to being very soluble in polar solvents, this complex was found to be slightly soluble in *n*-hexane.

Chlorodicarbonyltris(trimethylphosphite)manganese(I):-

A mixture of $Mn(CO)_5Cl$(1.01g) and $P(OMe)_3$(1.90g) in 100ml of chloroform was refluxed for 8hr. The product was obtained as above, and recrystallized at room temperature from *n*-hexane to give a bright yellow complex. (Yield: 1.55g, 69%; mp: 143-145°.) *Anal.* Calcd for $C_{11}H_{27}O_{11}P_3MnCl$: C, 25.47; H, 5.25; P, 17.92; Cl, 6.84. Found: C. 25.59; H, 4.92; P, 15.94; Cl, 7.58. In the ^1H n.m.r. spectrum, a multiplet centered at τ = 6.24p.p.m. was observed, caused by phosphorous-proton(CH_3) coupling.

Bromodicarbonyl(trimethylphosphite)[1, 2-bis(diphenylphosphino)ethane]-manganese(I).½ Chloroform:-

A chloroform solution (20ml) containing 0.54g of *cis*-$Mn(CO)_2[P(OMe)_3]_3Br$ and 0.50g of diphos was refluxed for 9hr. The usual work-up procedure was followed to obtain the orange product (Yield: 0.27g, 32%.) *Anal.* Calcd for $C_{31.5}H_{33.5}O_5P_3MnBrCl_{1.5}$: C, 48.94; H, 4.33; P, 10.64. Found: C, 48.61; H, 4.37; P = 12.02.

Chlorodicarbonyl(trimethylphosphite)[1, 2-bis(diphenyphosphino)ethane]-manganese(I)Chloroform:-

A mixture of *cis*-$Mn(CO)_2[P(OMe)_3]_3Br$(0.447g) and diphos(0.390g) in 15ml of chloroform was refluxed for 4.5hr. On cooling, 40ml of *n*-hexane were added and the volume reduced to 5ml. The resulting precipitate was recrystallized as yellow crystals from *n*-hexane and dried *in vacuo* (4hr).

(Yield: 0.41g, 60%; mp: 172-174°.) *Anal.* Calcd for $C_{32}H_{34}O_5P_3MnCl_4$: C, 48.80; H, 4.32; P, 11.7; Cl, 18.02. Found: C, 49.04; H, 4.43; P, 11.82; Cl, 17.40.

In the ^1H n.m.r. spectrum, two resonances of equal intensity centered at τ = 6.37p.p.m. were observed, caused by phosphorous-proton(CH_3) coupling, J_{PH} = 11 c.p.s.

Bromodicarbonyltris(triallylphosphite)manganese(I):-

A mixture of $Mn(CO)_5Br$(0.54g) and triallylphosphite (1.75g) in chloroform (40ml) was refluxed for 23hr. After removal of the solvent, precipitation by *n*-hexane at room, ice, and dry-ice temperatures was attempted but met with no success. Chromatography on an alumina column using *n*-hexane as eluent was therefore used to wash away any excess $P(OCH{:}CHCH_3)_3$, and the dark orange "oil" obtained after removal of volatile material was pumped on for 5hr. *Anal.* Calcd for $C_{29}H_{45}O_{11}P_3MnBr$: C, 43.68; H, 5.69; P, 11.65; Br, 10.02. Found: C, 43.97; H, 6.08; P, 11.45; Br, 10.09.

Bromodicarbonyl(triphenylphosphite)[1, 2-bis(diphenylphosphino)ethane]manganese(I):-

A chloroform solution (40ml) containing 1.10g of *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$, 1.3g of diphos, and 6.4g of $P(OPh)_3$ was refluxed for 100min. The reaction was then stopped and the solvent was removed by means of a water aspirator. The resulting "oil" was mixed with 2ml of chloroform and chromatographed on an alumina column using petroleum ether (30-60°) followed by a benzene: petroleum ether (1:1) mixture as eluent. The initial yellow portion leaving the column contained the desired product which was obtained by removing the solvent, and recrystallizing from *n*-hexane. The product was then dried *in vacuo*. (Yield: 0.28g, 24%; mp: 159-161°.) *Anal*. Calcd for $C_{46}H_{39}O_5P_5MnBr$: C, 61.42; H, 4.37; P, 10.33; Mn, 6.11; Br, 8.88. Found: C, 61.44; H, 4.67; P, 9.91; Mn, 6.47; Br, 9.06. *Mol. wt.* Calcd: 900. Found: 917.

Bromodicarbonyl(triphenylphosphite)(o-phenylenebisdiphenylarsine)manganese(I):-

A mixture of *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$(1.01g), diars(1.00g), and $P(OPh)_3$(2.6g), was refluxed in 50ml of chloroform under nitrogen. The product was isolated *via* a work-up similar to the one described for the previous complex. (Yield: 0.15g, 16%, mp: 154-156°.) *Anal*. Calcd for $C_{30}H_{31}O_5As_2PMnBr$: C, 45.77; H, 3.97; As, 19.03; Br. 10.15. Found: C, 46.14; H, 4.02; As, 18.81; Br, 10.87.

Bromodicarbonyl(triphenylphosphite)(2,2'-dipyridyl)manganese(I):-

A chloroform solution (40ml) containing 1.445g of *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$, 0.41g of dipy, and 2.3g of $P(OPh)_3$ was refluxed for 48hr under nitrogen. The chloroform was then removed by a stream of nitrogen, and the resulting "oil" chromatographed on alumina, using, first benzene, followed by a benzene: chloroform (2:1) mixture. The desired product was the *second* species developed on the column and was eluted using ethanol. Evaporation of the eluent gave the product which was a dark orange "oil" at room temperature and could not be induced to crystallize.

Bromodicarbonyl(triphenylphosphite) [1, 2-bis(diphenylarsino)ethane]manganese(I):-

A mixture of *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$(1.06g), diarsine(1.20g), and $P(OPh)_3$(2.00g), was refluxed in 50ml of chloroform for 5hr after which the reaction was stopped and all volatile matter removed on a water aspirator. The resulting "oil" was mixed with 2ml of chloroform and chromatographed on alumina, using petroleum ether (30-60°), followed by a benzene: petroleum ether (3:1) mixture. The solvent was removed and the dicarbonyl product was recrystallized in the form of yellow crystals from *n*-hexane and dried *in vacuo*.

Bromotricarbonyl[bis(2-diphenylphosphino)phenylphosphine]manganese(I):-

A chloroform solution (60ml) containing $Mn(CO)_5Br$ (0.734g) and triphos (1.438g) was refluxed for 80min, after which the chloroform was removed on a water aspirator. The yellow product was precipitated from a dichloromethane solution using absolute ethanol, and dried *in vacuo*. (Yield: 1.3g, 68%; mp: 127-130°.) *Anal.* Calcd for $C_{37}H_{29}O_3P_3MnBr$: C, 58.98; H, 4.41; P, 12.33; Mn, 7.29; Br, 10.61. Found: C, 57.93; H, 4.54; P, 12.10; Mn, 7.53; Br, 11.03.

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PART IV

KINETIC STUDIES OF SOME REACTIONS OF SUBSTITUTED HALOCARBONYLMANGANESE(I) DERIVATIVES

I. THERMAL DECOMPOSITION OF *trans*-$Mn(CO)_3(PPh_3)_2X$ (X = Cl, Br, I)

II. REACTIONS OF *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$) WITH BIDENTATES

CHAPTER I KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION REACTIONS OF THE *trans*-BIS(TRIPHENYLPHOSPHINE)-MANGANESE TRICARBONYL HALIDES[*]

A. INTRODUCTION

Mechanistic studies of the substitution reactions of metal carbonyl complexes have been mainly concerned with the replacement of carbonyl groups by other ligands.[1] Recently, however, there has been increased interest in reactions involving the replacement of ligands other than carbonyl attached to metal atoms.[1-15]

In one of these studies, Darensbourg and Brown[13] reported kinetic data for the thermal decomposition of $Mo(CO)_5(C_5H_{10}NH)$ to form $Mo(CO)_6$ and proposed that the decomposition proceeded by the two-step mechanism shown in equations 1 and 2.

$$Mo(CO)_5(C_5H_{10}NH) \xrightarrow{slow} Mo(CO)_5 + C_5H_{10}NH \qquad (1)$$

$$Mo(CO)_5 + Mo(CO)_5(C_5H_{10}NH) \xrightarrow{fast} Mo(CO)_6 + Mo(CO)_4(C_5H_{10}NH)\,(?) \qquad (2)$$

The net result of the decomposition was the replacement of piperidine by CO. In this section, the results of an investigation on the kinetics of the thermal decomposition of the *trans*-$Mn(CO)_3(PPh_3)_2X$ (X = Cl, Br, I) derivatives (A) in *s*-tetrachloroethane at 40-60° to give *cis*-$Mn(CO)_4(PPh_3)X$ will be presented, and a possible mechanism suggested. In these reactions too, a coordinated ligand is substituted by CO as the net result.

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[*] The contents of this Chapter have been published, see H.K. Spendjian and I.S. Butler, *Inorg. Chem.*, 9, 1268(1970).

B. EXPERIMENTAL SECTION

The *trans*-$Mn(CO)_3(PPh_3)_2X$ complexes were prepared by maintaining a chloroform solution of the appropriate $Mn(CO)_5X$ complex and a five to tenfold excess of PPh_3 at 60-80° until the i.r. spectrum of the reaction mixture in the CO stretching region corresponded principally to that of the desired product. (A small amount of *cis*-$Mn(CO)_4(PPh_3)X$ was almost always present at this time.) The products were retrieved from solution by following the method outlined in the literature for similar complexes,[16] and recrystallized until analytically pure.

The *s*-tetrachloroethane was purified as described in the literature.[17]

Kinetic data were obtained by monitoring the rate of decrease of the lowest energy CO stretching absorption of each substrate ($\sim$1914cm^{-1}) using a Perkin Elmer model 337 grating infrared spectrophotometer. Solutions of the substrates were prepared in aluminum foil-wrapped[18] schlenk tubes fitted with neoprene serum caps and thermostated in a constant temperature bath. Samples were withdrawn with a syringe at appropriate intervals and their spectra scanned in the CO stretching region. The rate of decomposition of *trans*-$Mn(CO)_3(PPh_3)_2Br$ at 50.0° was also measured by following the rate of decreasing absorbance of the band at 449mμ in the visible spectrum. The rates obtained by the two different methods were virtually identical. The visible spectra were recorded on a Coleman-Hitachi model 124u.v.-visible spectrophotometer coupled to an external recorder.

Linear first order plots of ln $(A-A_\infty)$, where A is the absorbance at time t and A_∞ is the absorbance at infinite time, *vs.* t

were obtained. The reactions went to completion and the plots were linear to 75-85% completion, except for *trans*-$Mn(CO)_3(PPh_3)_2I$ for which significant deviations began to appear after 50% completion. In the latter case the reaction product, *cis*-$Mn(CO)_4(PPh_3)I$, was decomposing further to form $Mn(CO)_5I$ presumably with regeneration of the starting material, *trans*-$Mn(CO)_3(PPh_3)_2I$.

The rate constants were calculated using a least squares computer program and are considered to be accurate to about ±10%.

C. RESULTS AND DISCUSSION

The observed rate constants (k_{obsd}) given in Table I indicate a first-order dependence on substrate concentration. Sample spectra in a typical kinetic run are shown in Figure 1, while a typical plot of $\ln(A-A_\infty)$ *vs.* t is given in Figure 2. These experimental results are in accord with the mechanism shown in equations 3 and 4 involving the rupture of an Mn-P bond as the slow rate-determining step.

$$\textit{trans}\text{-}Mn(CO)_3(PPh_3)_2X \xrightarrow{k_1} Mn(CO)_3(PPh_3)X + PPh_3 \qquad (3)$$

$$Mn(CO)_3(PPh_3)X + \textit{trans}\text{-}Mn(CO)_3(PPh_3)_2X \xrightarrow{\text{fast}}$$
$$\textit{cis}\text{-}Mn(CO)_4(PPh_3)X + Mn(CO)_2(PPh_3)_2X\ (?) \qquad (4)$$

Provided that the decomposition reactions go to completion, the observed rate constant will be given by $k_{obsd} = 2k_1$. The mechanism is supported by the activation parameters (Table I, footnotes a, b, and f) which are in the range expected for an S_N1 dissociative mechanism.[1] This mechanism is similar to that proposed by Darensbourg and Brown[13] for the decomposition of $Mo(CO)_5(C_5H_{10}NH)$ (equations 1 and 2).

None of the CO bands observed in any of the i.r. spectra of the reaction mixtures taken during the kinetic runs were attributable to dicarbonyl species of the type $Mn(CO)_2(PPh_3)_3X$. It appears that either these dicarbonyl species or the intermediates, $Mn(CO)_2(PPh_3)_2X$, rapidly decomposed under the experimental conditions employed. In agreement with the proposed mechanism, the yield (calculated from a Beer's law plot) of *cis*-$Mn(CO)_4(PPh_3)Br$ always represented 40-50% of the concentration of the starting material, *trans*-$Mn(CO)_3(PPh_3)_2Br$. Furthermore, as expected, the rate of decomposition was retarded by the presence of excess PPh_3

TABLE I. FIRST ORDER RATE CONSTANTS FOR THE DECOMPOSITION REACTIONS OF *trans*-$Mn(CO)_3(PPh_3)_2X$ IN *s*-TETRACHLOROETHANE

X in *trans*-$Mn(CO)_3(PPh_3)_2X$	10^3Concn, *M*	Temp. °C	$10^4 k_{obsd}$, sec^{-1}
Cl[a]	3.79	40.0	0.89
	3.86	50.0	3.3
	6.95		2.7
	2.82	60.0	9.6
Br[b]	4.01	40.0	0.60
	1.34	50.0	2.9[c]
	1.50		2.8
	2.45		2.8
	2.36		2.8
	2.36		2.7[d]
	2.44		1.3[e]
	3.01		2.6
	4.72		2.0[d]
	4.80		2.3
	6.10		2.1
	6.59		2.2
	3.53	60.0	10
I[f]	3.54	40.0	0.65
	3.76	50.0	2.3
	5.20		2.0
	3.26	60.0	9.5

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[a] $\Delta H = 25 \pm 2$ kcal $mole^{-1}$ and $\Delta S = -4 \pm 4$eu.

[b] $\Delta H = 29 \pm 2$ kcal $mole^{-1}$ and $\Delta S = 10 \pm 4$eu.

[c] From following changes in the visible spectrum.

[d] In the presence of CO.

[e] In the presence of 0.0103*M* PPh_3.

[f] $\Delta H = 28 \pm 2$ kcal $mole^{-1}$ and $\Delta S = 5 \pm 4$eu.

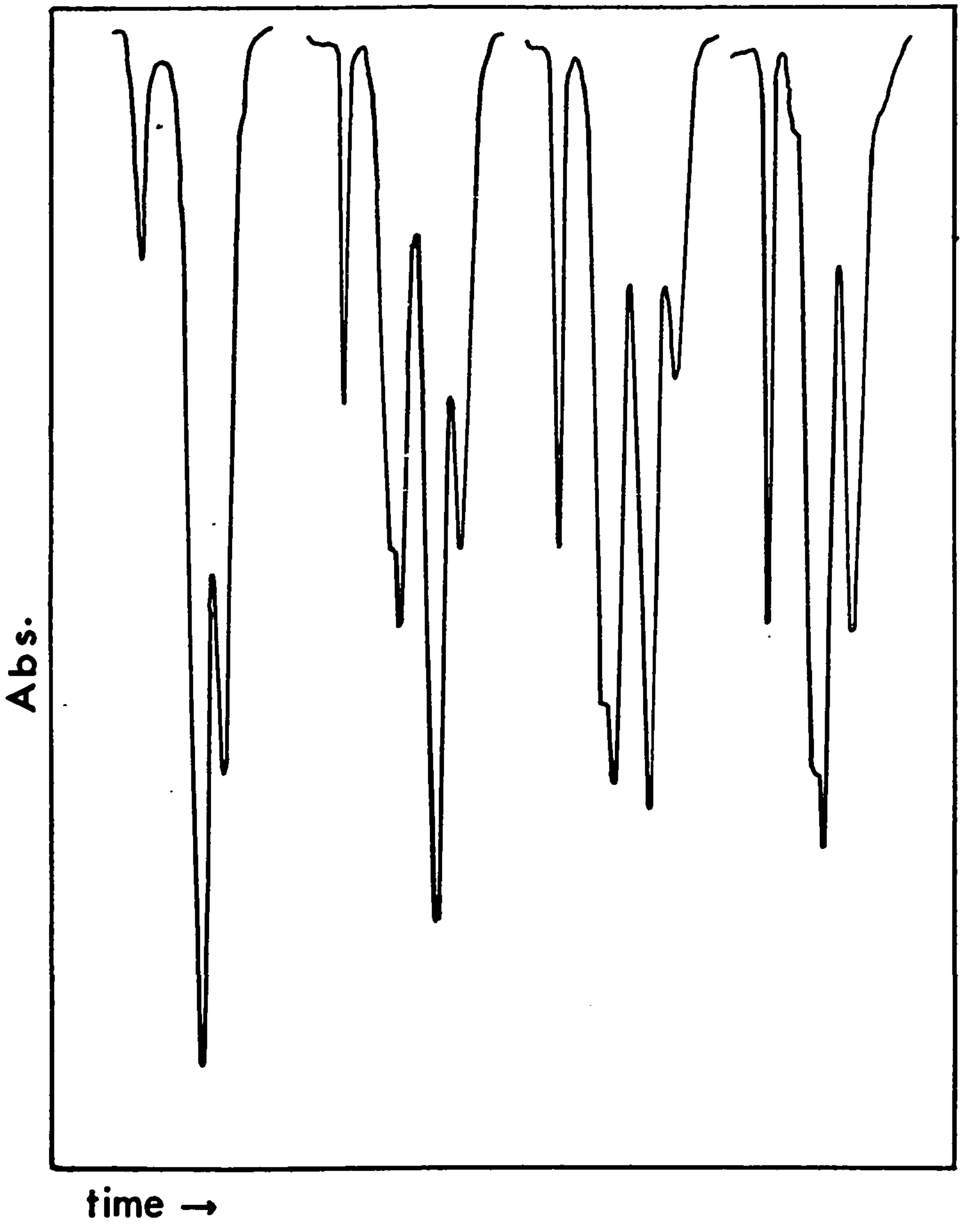

Figure 1.-Infrared spectra in the CO stretching region of the thermal decomposition of *trans*-$Mn(CO)_3(PPh_3)_2Br$ in *s*-TCE at 50°.

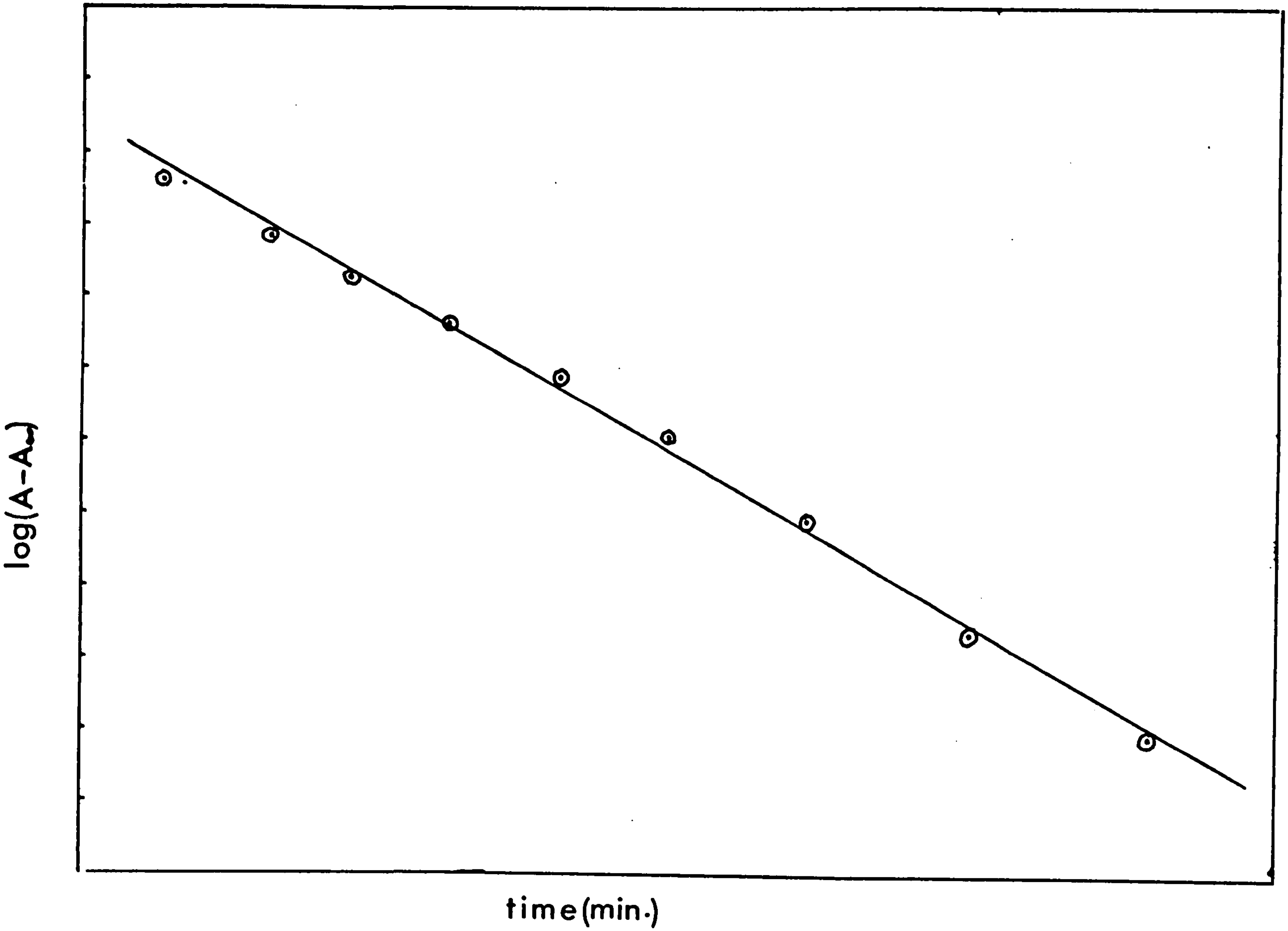

Figure 2.-First-order plot for the thermal decomposition of *trans*-Mn(CO)$_3$(PPh$_3$)$_2$Br in *s*-TCE at 50°.

(Table I, footnote e). When the decomposition of *trans*-$Mn(CO)_3(PPh_3)_2X$ was carried out under an atmosphere of CO the yield of *cis*-$Mn(CO)_4(PPh_3)Br$ increased from the usual 40-50% to about 85% without any apparent effect on the decomposition rate. The increased yield of *cis*-$Mn(CO)_4(PPh_3)Br$ presumably arises because CO successfully competes with a molecule of starting material for the intermediate $Mn(CO)_3(PPh_3)Br$, and so reaction 4 is no longer the only way in which *cis*-$Mn(CO)_4(PPh_3)Br$ can be formed.

Furthermore, if reaction 4 is diminished in the presence of CO, the rate of decomposition of *trans*-$Mn(CO)_3(PPh_3)_2Br$ should be slower than usual. That this was not observed is presumably because the decrease in decomposition rate was fairly small and fell within the limits of experimental error of the method used for rate determination.

On presenting these results for publication a referee suggested an alternative mechanism for the decomposition reactions that would be consistent with the observations discussed so far. This mechanism is shown in equations 5, 6, and 7 and involves two concomitant rate-determining steps: the rupture of an Mn-P bond and of an Mn-C bond. The observed rate constant for this mechanism (assuming that the reactions go to completion) will be given by $k_{obsd} = k_1 + k_2$.

$$\textit{trans}\text{-}Mn(CO)_3(PPh_3)_2X \xrightarrow{k_1} Mn(CO)_3(PPh_3)X + PPh_3 \qquad (5)$$

$$\textit{trans}\text{-}Mn(CO)_3(PPh_3)_2X \xrightarrow{k_2} Mn(CO)_2(PPh_3)_2X\ (?) + CO \qquad (6)$$

$$Mn(CO)_3(PPh_3)X + CO \xrightarrow{fast} \textit{cis}\text{-}Mn(CO)_4(PPh_3)X \qquad (7)$$

However, when the decomposition of *trans*-$Mn(CO)_3(PPh_3)_2Br$ was studied in the presence of $C^{18}O$ the substrate i.r. band at 1951cm^{-1} was observed to disappear qualitatively at a much faster rate than normal and a band due to a $C^{18}O$-substituted species rapidly appeared at approximately $1930cm^{-1}$. These observations suggest that the rate of CO substitution is significantly faster than the rate of decomposition and therefore we favour our proposed mechanism over that indicated by the referee.

In sharp contrast to the rates of the CO substitution reactions of $Mn(CO)_5X$[19,20] and *cis*-$Mn(CO)_4LX$[21] [L = PPh_3, $SbPh_3$, etc] which decrease dramatically with changes in X in the order Cl > Br > I, the rates of the decomposition reactions of *trans*-$Mn(CO)_3(PPh_3)_2X$ were little affected by changes in X. The decrease in the CO substitution rates with the increasing atomic weight of X has been explained in terms of the electronegativities of the X atoms - the lower the electronegativity of the X atom, the greater the electron density on the manganese atom available for back-bonding to the carbonyl groups, and consequently the stronger the Mn-C bonds. If the Mn-P bond strengths in the *trans*-$Mn(CO)_3(PPh_3)_2X$ compounds are significantly dependent on π-bonding, it would be reasonable to expect the observed decomposition rates to show some dependence on X. However, as this was not found to be the case, it appears that the Mn-P bond strengths in the tricarbonyl halides stem mainly from σ- rather than π-bonding effects. Other workers have reached the same conclusion concerning the Mo-P,[5] W-P,[10,12] and Ni-P[14] bond strengths in molybdenum, tungsten, and nickel carbonyl complexes.

The thermal decomposition of *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$ was also studied. However, contrary to what would be predicted from the lower basicity and resultant poorer σ-bonding ability of $P(OPh)_3$ by comparison with PPh_3,[12] the reaction proceeded extremely slowly ($t_{\frac{1}{2}}$ >> 24 hr). $P(OPh)_3$ has also been found to be anomalous in its behaviour in the substitution reactions of *trans*-$Mo(CO)_4L_2$[L = $P(OPh)_3$ and PPh_3].[9]

In an effort to extend the study, the synthesis of *trans*-$Mn(CO)_3$-$(SbPh_3)_2Br$ was attempted. However, only the *cis*-complex could be isolated, contrary to what had been previously predicted.[16] Dobson and Houk[9] have recently found that substituted molybdenum carbonyls tend to form *cis*-complexes with $SbPh_3$ and *trans*-complexes with PPh_3 and $AsPh_3$ and attributed the difference to the larger size of the Sb atom. Heating a solution of *cis*-$Mn(CO)_3(SbPh_3)_2Br$ did afford *cis*-$Mn(CO)_4(SbPh_3)Br$ but the decomposition appears to be much more complex than the decomposition of the *trans*-$Mn(CO)_3(PPh_3)_2X$ compounds, as a simple rate plot was not obtained.

CHAPTER II KINETIC STUDIES OF THE REACTIONS BETWEEN SUBSTITUTED BROMOPENTACARBONYLMANGANESE(I) COMPLEXES AND BIDENTATES

A. INTRODUCTION

While attempting to prepare manganese dicarbonyl complexes by the reaction of *cis*-$Mn(CO)_4LBr$ complexes with the bidentate ligand diphos, it was observed that instead of eliminating two CO groups, the bidentate ligand invariably eliminated one CO group and the L group. This resulted in the formation of *cis*-$Mn(CO)_3(diphos)Br$. The overall general reaction is shown in equation 8.

$$cis\text{-}Mn(CO)_4LBr + A\text{-}A \longrightarrow cis\text{-}Mn(CO)_3(A\text{-}A)Br + CO + L \qquad (8)$$

This reaction presented the interesting aspect of having only one carbonyl product in contrast to the reactions of the *trans*-$Mn(CO)_3L_2X$ complexes with bidentates, which, as detailed in Part III, form two carbonyl products. Furthermore, preliminary investigations indicated that the rate was, in certain cases, dependent on both the nature and the concentration of the entering bidentate ligand.

Angelici and Basolo[21] have reported kinetic studies of the reaction shown in equation 9.

$$cis\text{-}Mn(CO)_4LX + L' \longrightarrow cis\text{-}Mn(CO)_3LL'X + CO \qquad (9)$$

They found that the rates were first order in substrate and independent of the nature and concentration of the monodentate ligands, L', but dependent on the nature of L. A simple dissociation mechanism was therefore proposed to explain the results.

In view of Angelici and Basolo's data and the results of the preliminary investigation of reaction 8, it was clear that very different mechanisms were operational when the entering ligand was monodentate or bidentate. The initial conclusion was reached that, for the various bidentates, either a number of totally different mechanisms were at play, or, the same mechanism was in effect in all cases, but with a bidentate dependent step.

A number of kinetic studies have been reported on the substitution of ligands other than CO in octahedral carbonyl complexes by bidentate ligands. For example, Zingales, Canziani, and Basolo[5] have reported data for the reaction shown in equation 10.

$$\textit{cis/trans}\text{-Mo(CO)}_4\text{L}_2 + \text{diphos} \longrightarrow \text{Mo(CO)}_4\text{(diphos)} + 2\text{L} \quad (10)$$

They found that the rates were first order in substrate and independent of the concentration of diphos. A mechanism was proposed in which the slow rate-determining step was the loss of L. This step was followed by a rapid attack on molybdenum by the entering diphos and then the second L was eliminated to give the final product. The order of reactivity which decreased as $PCl_3 >> PClPh_2 > PPh_3 >> P(OPh)_3$, led to the conclusion that the Mo-P bond strength was primarily due to σ-bonding.

In a somewhat later report, Graziani, Zingales, and Belluco[7] discussed the kinetic data for a reaction similar to that shown in equation 10, but using dipy instead of diphos as the entering ligand, and a larger variety of substrates. The same reaction mechanism was proposed, but it was concluded that the order of decreasing reactivity with changing L which was $PCl_3 >> py >> C_8H_{12} \sim AsPh_3 > PPh_3 > PCl_2Ph >> SbPh_3 >> CO$, indicated that the π-bonding ability of the ligands played a significant part in the M-L bond strength.

More interesting from the point of view of the mechanism involved, at least with respect to the present work, are the reports[5,6] on the reaction shown in equation 11. In this case the reaction was found to depend both

$$Mo(CO)_4C_8H_{12} + 2L\ (or A\text{-}A) \longrightarrow Mo(CO)_4L_2 [or\ Mo(CO)_4A\text{-}A] + C_8H_{12} \qquad (11)$$

on the nature and the concentration of the entering ligand. A plot of the observed rate constant, k_{obsd}, *versus* the concentration of the entering ligand showed that the rates of reaction increased linearly with increasing concentration of nucleophile. Furthermore the plots extrapolated to approximately the same non-zero value. To explain the concentration dependence two mechanisms were proposed. The simpler one was that a direct S_N2 displacement by L(or A-A) was taking place to yield the product. Such a path had been previously suggested for $Mo(CO)_6$.[22] The alternative mechanism involved a rapid pre-equilibrium leading to an intermediate of lower coordination number. The general scheme is shown in Figure 3. The two species (II and IV) shown as being less than six-coordinated were explained as being possibly solvated. Using the steady-state approximation for this scheme k_{obsd} is given by equation 12.

$$k_{obsd} = k_1 \frac{k_2 + k_3[L]}{k_{-1} + k_2 + k_3[L]} \qquad (12)$$

Assuming that $k_3[L]$ was negligible in comparison to k_{-1} at concentrations of L used, and that k_2 was comparable to $k_3[L]$, the approximate two-term rate law in equation 13 was obtained.

$$k_{obsd} = k' + k''[L] \qquad (13)$$

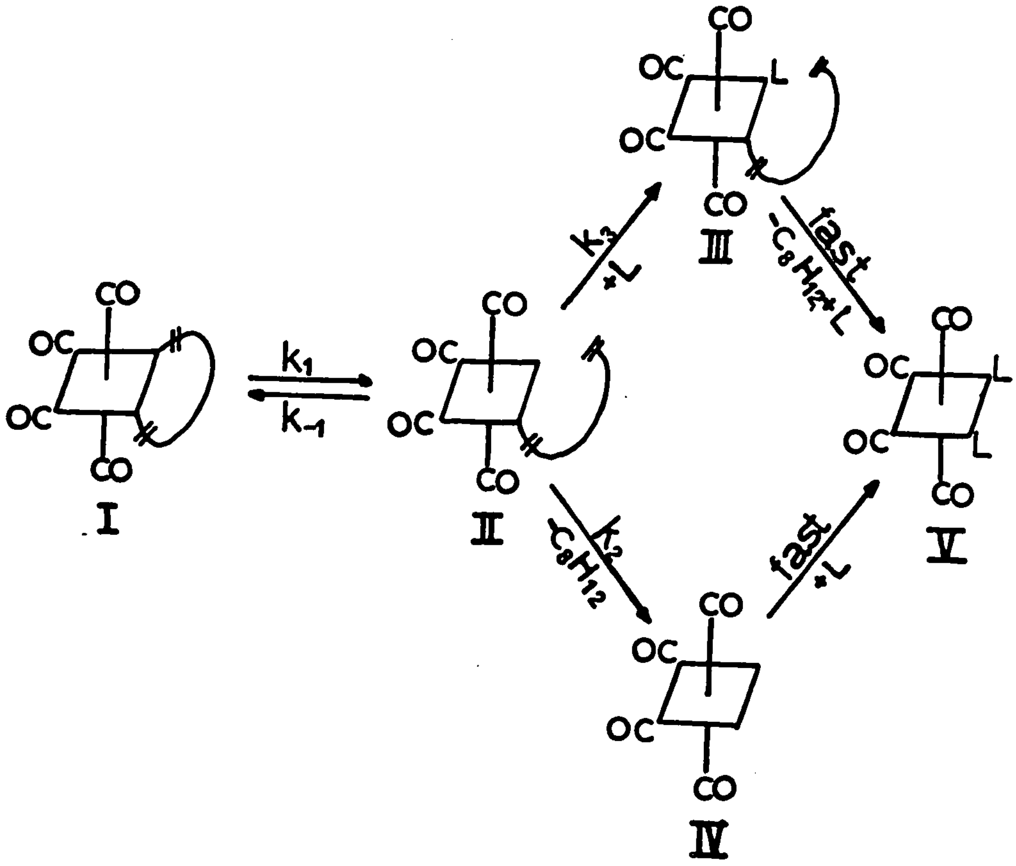

Figure 3.-Mechanism for the reaction of $Mo(CO)_4C_8H_{12}$ with L(or A-A).

When [L] is close to zero, equation 12 reduces to equation 14, thus accounting for the non-zero intercept.

$$k_{\text{obsd}} = \frac{k_1 k_2}{k_{-1} + k_2} \tag{14}$$

From equation 12 and following the above assumptions it would be expected that a decrease in the dependence of the reaction rate on the concentration of L(or A-A) would occur at higher concentration, and a limiting rate, would be observed. That this was not found to be the case was explained as possibly being due to the fact that both the scheme in Figure 3 and the direct S_N2 mechanism were making a contribution to the concentration dependent term. Otherwise, the limiting rate may have been reached even at the lowest concentration of L used, providing that (II) reacted rapidly compared to chelate ring closure, k_2 and/or $k_3 \gg k_{-1}$. Thus, the extrapolated values of k_{obsd} at [L] = zero, corresponded to either k_1 or the combination of rate constants given in equation 14.

Until recently, first row transition metal carbonyl complexes were believed not to readily undergo S_N2 displacement processes. For example, in the reaction of the Group VIB hexacarbonyls, $M(CO)_6$, with various ligands, the contribution of the S_N2 mechanism in the chromium complex[23] was virtually negligible while it played an important role in the reactions of the molybdenum and tungsten complexes.[22,23] Also, the substitution reactions of the *o*-phen,[24] and dipy,[25] complexes of $Cr(CO)_6$, $Cr(CO)_4$(*o*-phen) and $Cr(CO)_4$(dipy), were found to proceed only *via* an S_N1 path while the similar Mo and W complexes obeyed a two term rate law.[26,27] Recently, however, Dobson[28] has studied the reactions of triphenylmetalpentacarbonylmanganese(0) **complexes**, $Ph_3EMn(CO)_5$ (E = Si, Ge, Sn, Pb), with Lewis bases and found that the reactions of the Ge and Sn complexes with L in decalin at 150-190° to give $Ph_3EMn(CO)_4L$ proceeded according to a two-term rate law. He suggested that the reactions proceeded by two competing mechanisms; one in which the rate-determining step was the dissociation of CO (ligand independent path), the other in which nucleophilic attack of L on the substrate (ligand dependent path) to give a heptacoordinated intermediate was the rate-determining step.

In this chapter, the results of an investigation of the kinetics of the reaction shown in equation 8 are reported. The complexes studied contained the leaving groups PPh_3, $AsPh_3$, and $SbPh_3$; while the entering bidentate ligands used were diphos, diarsine, and dipy.

B. EXPERIMENTAL

i. Preparation of Substrates

The *cis*-$Mn(CO)_4LBr$ (L = PPh_3, $AsPh_3$, $SbPh_3$) complexes were prepared by refluxing chloroform solutions of $Mn(CO)_5Br$ and a slight excess of the appropriate ligand until the i.r. spectra of the reaction mixtures indicated that all the $Mn(CO)_5Br$ had reacted. As reported in the literature,[20] the complexes were obtained by first evaporating the volatile matter, followed by recrystallization from *n*-hexane at dry-ice temperatures.

The complex *cis*-$Mn(CO)_4(PPh_3)Br$ was analyzed. Calcd for $C_{22}H_{15}O_4PMnBr$: C, 51.90; H, 2.97; Br, 15.69. Found: C, 52.11; H, 3.09; Br, 15.54.

ii. Kinetic Studies

Kinetic data were obtained by monitoring the rate of decrease of the high-frequency CO stretching absorption near $2100cm^{-1}$ of the substrates in chloroform solution in a manner similar to that detailed in the preceding chapter on the thermal decomposition reactions. All the kinetic runs were carried out under pseudo-first-order conditions. The reaction vessels were wrapped in aluminium foil to exclude light. The first-order plots were linear to better than 75% completion, apart from that for the reaction between *cis*-$Mn(CO)_4(AsPh_3)Br$ and diarsine which showed deviations from linearity after about one half-life.

The chloroform used in the kinetic runs was dried over calcium chloride and distilled and stored under nitrogen.

iii. Identification of the Products

The compound *cis*-$Mn(CO)_3(diphos)Br$ was isolated from a reaction mixture of 0.081g of *cis*-$Mn(CO)_4(PPh_3)Br$ and 0.068g of diphos in 10ml of chloroform. After the solution was allowed to stand for 5hr at room temperature, its volume was reduced to 2ml in a stream of air. These were added to 40ml of *n*-hexane causing the precipitation of the yellow product, which was then washed with *n*-hexane and dried in air. *Anal.* Calcd for $C_{29}H_{24}O_3P_2MnBr$: C, 56.42; H, 3.92; Br, 12.94. Found: C, 56.67; H, 4.09; Br, 12.74.

The infrared spectrum in chloroform solution afforded three strong bands at 2025, 1959, and 1919cm^{-1} in the CO stretching region. These were at identical positions to the bands of *cis*-$Mn(CO)_3(diphos)Br$ prepared by the direct action of diphos on $Mn(CO)_5Br$. The two complexes *cis*-$Mn(CO)_3(diarsine)Br$ and *cis*-$Mn(CO)_3(dipy)Br$ were identified by their infrared spectra which were very similar to that of the diphos complex. The CO stretching frequencies observed are as follows, *cis*-$Mn(CO)_3(diarsine)Br$: 2026, 1957, and 1919cm^{-1}; and *cis*-$Mn(CO)_3(dipy)Br$: 2033, 1945, and 1924cm^{-1}.

C. RESULTS AND DISCUSSION

The pseudo-first-order observed rate constants (k_{obsd}) are given in Tables II, III, and IV. The contents of these tables may be summarized as follows:

cis-$Mn(CO)_4(PPh_3)Br$ (Table II):- For this substrate different rates were obtained for the three bidentates used. In the reaction with diphos, k_{obsd} is seen to be independent of the diphos concentration; but when diarsine or dipy are the incoming ligands the rates are dependent on their concentrations. Notwithstanding the latter, k_{obsd} for the various bidentates is in the order diphos > diarsine > dipy.

cis-$Mn(CO)_4(AsPh_3)Br$ (Table III):- In this case the rates are seen to be independent both of the nature and the concentration of the bidentate ligands. As was mentioned in the Experimental section the reaction with diarsine afforded first-order plots which showed deviations after about one half-life. However, when only the initial points were taken into account, k_{obsd} was found to be very close to that observed with diphos and dipy.

cis-$Mn(CO)_4(SbPh_3)Br$ (Table IV):- The rate constants for the reactions of this substrate with diphos and dipy are seen to be equal and independent of the concentrations of the bidentates. On the other hand, the reaction with diarsine, although also concentration independent, is seen to be slightly slower than with the other two ligands.

Of the three substrates used, the most complex behaviour was observed for *cis*-$Mn(CO)_4(PPh_3)Br$ since it presented the widest variation in rate constants and concentration dependence. The reactions of this substrate will therefore be discussed in most detail. The reactions of

TABLE II. RATES OF REACTION OF *cis*-$Mn(CO)_4(PPh_3)Br$ WITH BIDENTATES IN CHLOROFORM

Bidentate	Conc. of *cis*-$Mn(CO)_4(PPh_3)Br$ $\times 10^3$ M	Conc. of bidentate, M	Temp. °C	$k_{obsd} \times 10^5$ sec^{-1}
diphos[a]	3.99	0.0392	25	19
	3.99	0.0511		18
	3.97	0.0217	30	40
	3.93	0.0552	35	80
	3.97	0.0630[b]		82
	3.85	0.0790		81
	3.95	0.1035		81
	2.14	0.1238		83
diarsine	3.97	0.0386	30.4	5.5
	3.95	0.0656		7.8
	3.95	0.0779		8.5
	3.75	0.0386	35	13
	3.91	0.0418[c]		11
	2.84	0.0569		19
	2.98	0.0765		23
	3.00	0.0964		25
	2.98	0.1163		30
	3.92	0.0383	40	18
	3.92	0.0576		25
	3.92	0.0744		27
dipy	3.99	0.0448	30.4	0.66
	3.99	0.0743		0.74
	3.99	0.1074		0.88
	3.99	0.1629		1.2
	3.99	0.2188		1.2
	3.87	0.0553	35	1.5
	3.99	0.1142		2.1
	3.97	0.1604		2.5
	3.99	0.2164		2.6
	3.94	0.0487	40	2.5
	3.94	0.0910		3.0
	3.94	0.1313		3.9
	3.94	0.1777		4.4
	3.94	0.2320		5.1

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[a] $\Delta H = 26.9 \pm 0.2$kcal mole^{-1}, $\Delta S = 1$leu.(The error in ΔH is a standard deviation)

[b] Also in the reaction mixture was PPh_3 at a concentration of 0.0348M.

[c] Also in the reaction mixture was PPh_3 at a concentration of 0.0358M.

TABLE III. RATES OF REACTION OF *cis*-$Mn(CO)_4(AsPh_3)Br$ WITH BIDENTATES IN CHLOROFORM

Bidentate	Conc. of *cis*-$Mn(CO)_4(AsPh_3)Br$ $\times 10^3$ *M*	Conc. of bidentate, *M*	Temp. °C	$k_{obsd} \times 10^5$ sec^{-1}
diphos[a]	3.58	0.0243	30	9.2
	4.50	0.0283	35	19
	3.40	0.0365		20
	3.42	0.0288	40	42
diarsine[b]	3.63	0.0377	30	8.8
	3.36	0.0250	35	17
	2.44	0.0564		19
	3.56	0.0350	40	36
	3.56	0.0548		36
dipy[c]	3.44	0.0743	30	11
	3.62	0.1356		11
	3.69	0.0437	35	21
	3.56	0.0513	40	43
	3.56	0.1045	46	46

[a] $\Delta H = 28.5 \pm 0.4$kcal $mole^{-1}$, $\Delta S = 13$eu.

[b] $\Delta H = 26.5 \pm 0.2$kcal $mole^{-1}$, $\Delta S = 6.5$eu.

[c] $\Delta H = 26.3 \pm 0.7$kcal $mole^{-1}$, $\Delta S = 6.2$eu.

TABLE IV. RATES OF REACTION OF *cis*-$Mn(CO)_4(SbPh_3)Br$ WITH BIDENTATES IN CHLOROFORM.

Bidentate	Conc. of *cis*-$Mn(CO)_4(SbPh_3)Br$ $\times 10^3$ *M*	Conc. of bidentate, *M*	Temp. °C	$k_{obsd}\times 10^5$ sec^{-1}
diphos[a]	3.52	0.0324	30	3.2
	2.83	0.0131	35	6.9
	3.70	0.0473		6.9
	2.10	0.0740		7.0
	3.37	0.0754	40	14
diarsine[b]	3.55	0.0378	30	2.1
	3.02	0.0383	35	4.7
	3.66	0.0400	40	10
	3.66	0.0514		10
	3.66	0.0599		10
dipy[c]	3.52	0.0645	30	3.2
	3.55	0.1364		3.3
	3.63	0.0850	35	7.1
	3.87	0.0756	40	15
	4.20	0.2090		15

[a] $\Delta H = 27.8 \pm 0.4$kcal $mole^{-1}$, $\Delta S = 8.8$eu.

[b] $\Delta H = 29.3 \pm 0.3$kcal $mole^{-1}$, $\Delta S = 13$eu.

[c] $\Delta H = 29.0 \pm 0.1$kcal $mole^{-1}$, $\Delta S = 13$eu.

the other two substrates will be discussed in perspective.

On comparing the ratio of k_{obsd} for the reactions of all three substrates with diphos, with the ratio of k_{obsd} found for the reactions of the type shown in equation 9,[21] it was noted that they were almost equal. Since the literature results were for *s*-TCE solutions, some of the reactions were re-examined in chloroform. The observed rate constants for the reactions of the PPh_3 and $AsPh_3$ substituted complexes with $P(OBu)_3$ were found to be the same, within experimental error, to the rate constants for the reactions with diphos.* (Contrary to previously published work,[21] in the case of *cis*-$Mn(CO)_4(SbPh_3)Br$, the infrared spectra of the reaction mixture recorded in the CO stretching region indicated the concomitant formation of *cis*-$Mn(CO)_4[P(OBu)_3]Br$. This therefore excluded the possibility of measuring the rate of CO dissociation for this substrate.) Thus, it seems safe to postulate that the same CO dissociation mechanism (Figure 4) is operational in both cases. The activation parameters for the reaction of *cis*-$Mn(CO)_4(AsPh_3)Br$ with diphos were calculated to be: $\Delta H = 28.5 \pm 0.4$ kcal $mole^{-1}$ and $\Delta S = 13.4$eu. In support of the proposed mechanism, these values compare favourably with those reported in the literature for the reaction of this substrate with monodentates: $\Delta H = 29.8 \pm 0.6$ kcal $mole^{-1}$ and $\Delta S = 17.8$eu. The slight differences presumably arise because of solvent effects.

When the k_{obsd} values for the reaction of *cis*-$Mn(CO)_4(PPh_3)Br$ with diarsine and dipy are plotted against the concentration of the bidentates, almost linear plots are obtained which curve at higher concentrations,

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* The rates of these reactions in chloroform were found to be about double those reported[21] for the reactions in *s*-TCE.

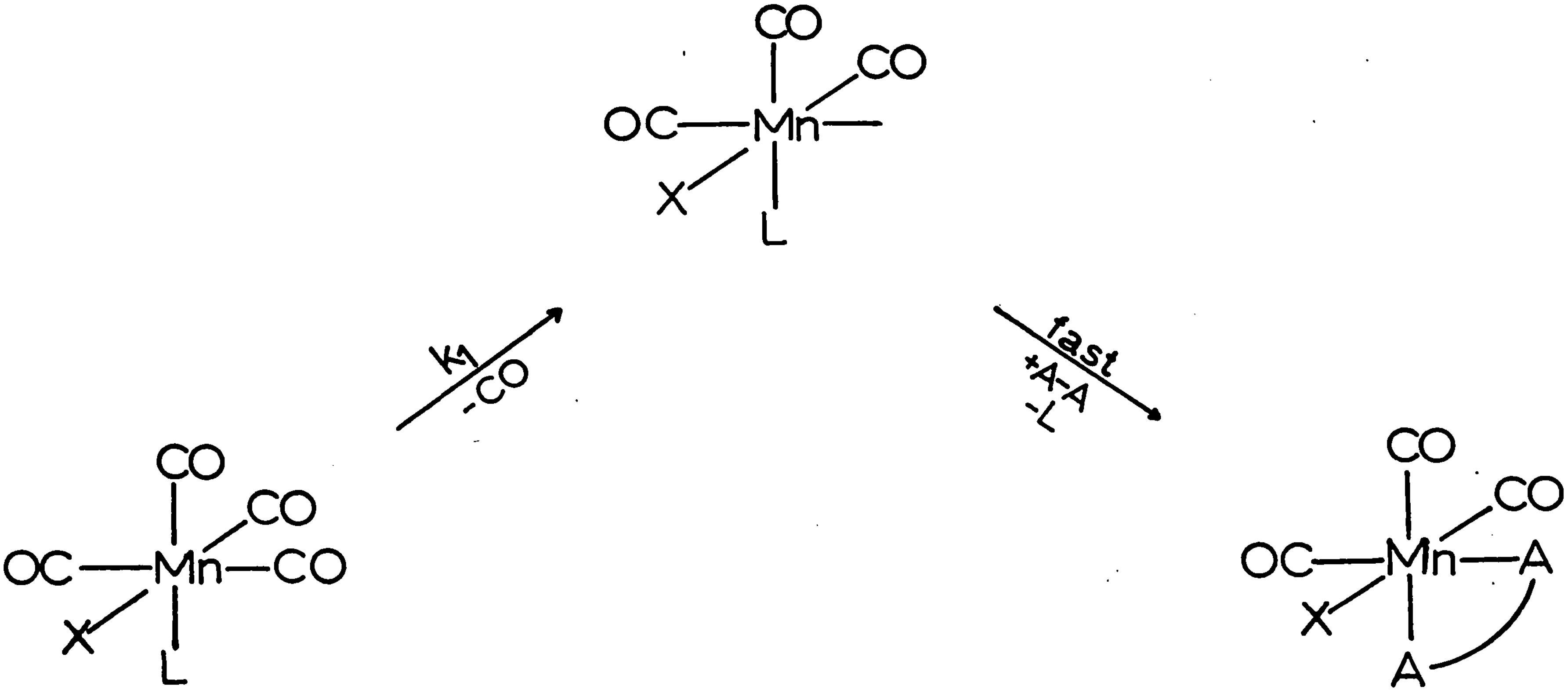

Figure 4.-Mechanism for the reaction of *cis*-Mn(CO)$_4$LBr with diphos.

particularly in the case of diarsine. Typical examples of the plots are shown in Figures 5 and 6. In the case of dipy (Figure 5), the intercept is definitely non-zero, but in the case of diarsine (Figure 6), it is difficult, due to the curvature and the steep slope, to decide whether the intercept is at the origin or at a small non-zero value.

Two mechanisms may be proposed to account for the concentration dependence. The first is a S_N2 displacement mechanism, while the second involves a rapid pre-equilibrium as shown in Figure 7. It is known from the reaction with diphos that reaction (I) → (II) shown in this figure does indeed occur; in that case however, the attack by diphos (k_3[A-A]) is very fast making the dissociation of CO the only rate-determining step. The contribution of the side step (I) → (V) probably plays no great part when diphos is used, as indicated by the fact that addition of excess PPh_3 did not retard the reaction.

By applying the steady-state approximation on the intermediates (II) and (V), the following general rate law may be derived,

$$\frac{\text{rate}}{[\text{I}]} = k_{obsd} = k_1 \frac{k_2 + k_3[\text{A-A}]}{k_{-1}[\text{CO}] + k_2 + k_3[\text{A-A}]} + k_4 \qquad (15)$$

Depending on the relative magnitudes of the various terms on the right-hand-side of equation 15, the following simpler expressions for k_{obsd} may be obtained which explain the observed kinetic data.

1. If k_2 is comparable to k_3[A-A], and both are negligible in comparison with k_{-1}[CO], equation 15 reduces to

$$k_{obsd} = \frac{k_1 k_2}{k_{-1}[\text{CO}]} + \frac{k_1 k_3[\text{A-A}]}{k_{-1}[\text{CO}]} + k_4 \qquad (16)$$

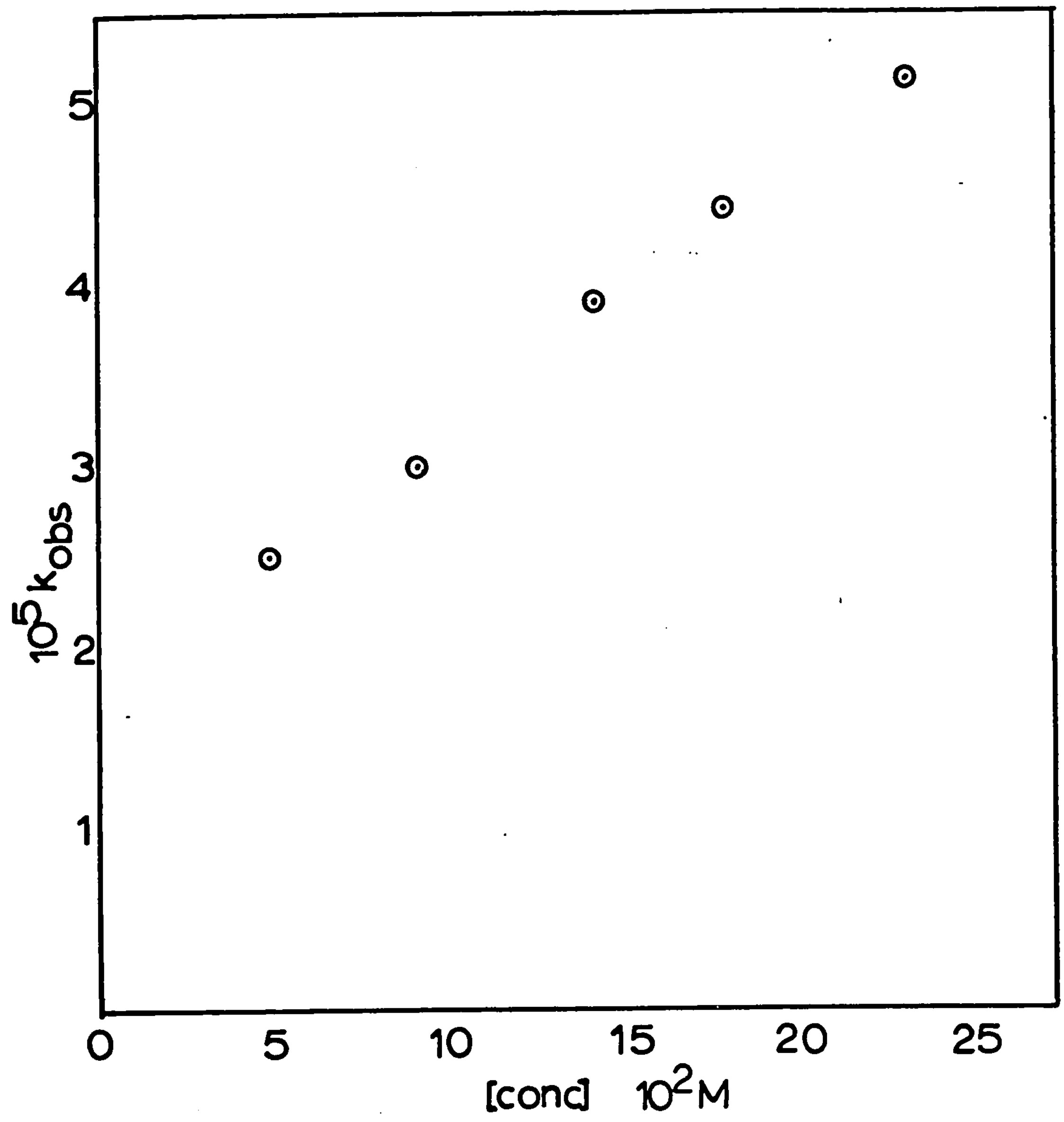

Figure 5.-Plot of the observed rate constants *vs.* the concentration of dipy for the reaction of *cis*-$Mn(CO)_4(PPh_3)Br$ with dipy in chloroform at 40°.

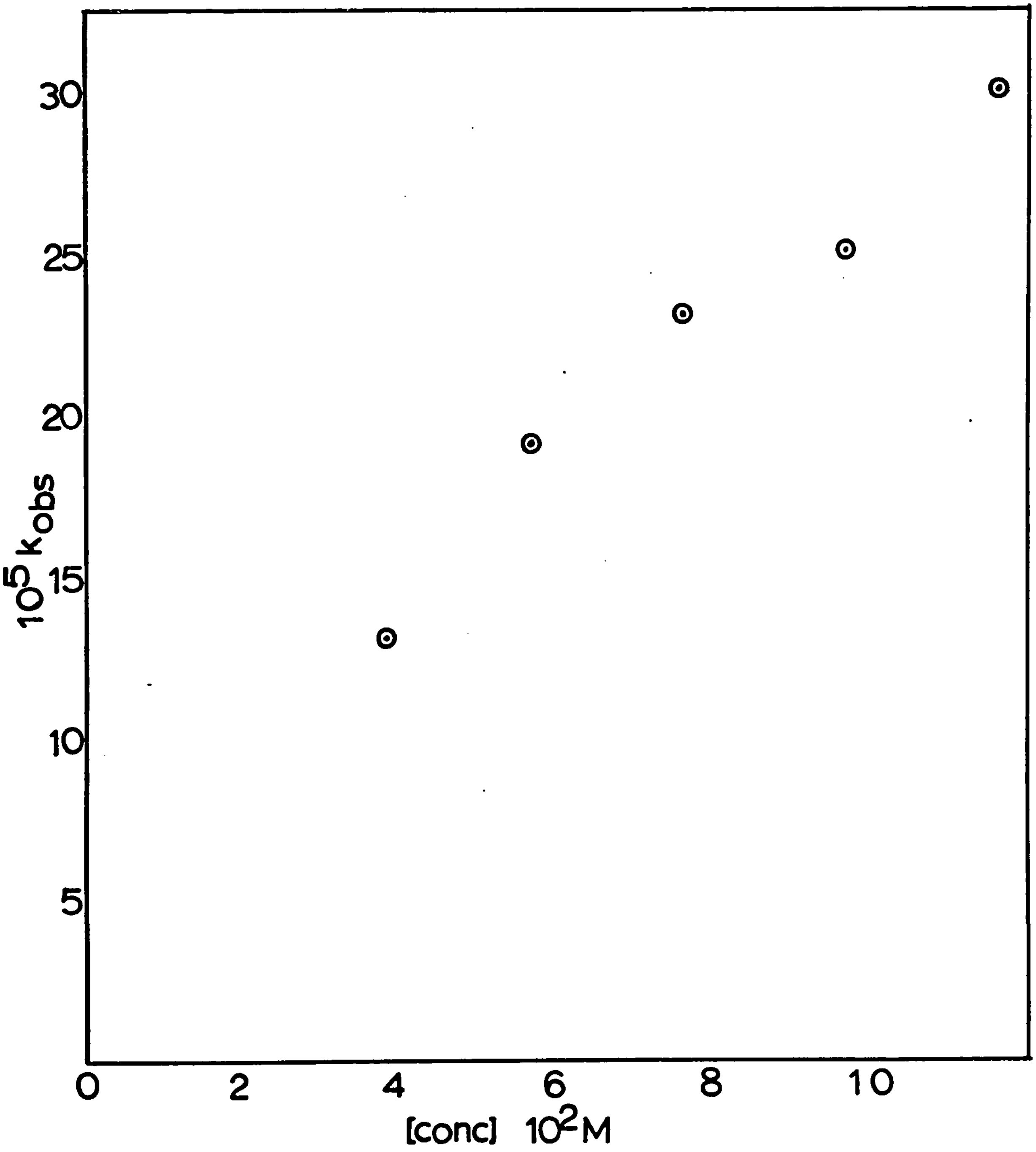

Figure 6.-Plot of the observed rate constants *vs.* the concentration of diarsine for the reaction of *cis*-$Mn(CO)_4(PPh_3)Br$ with diarsine in chloroform at 35°.

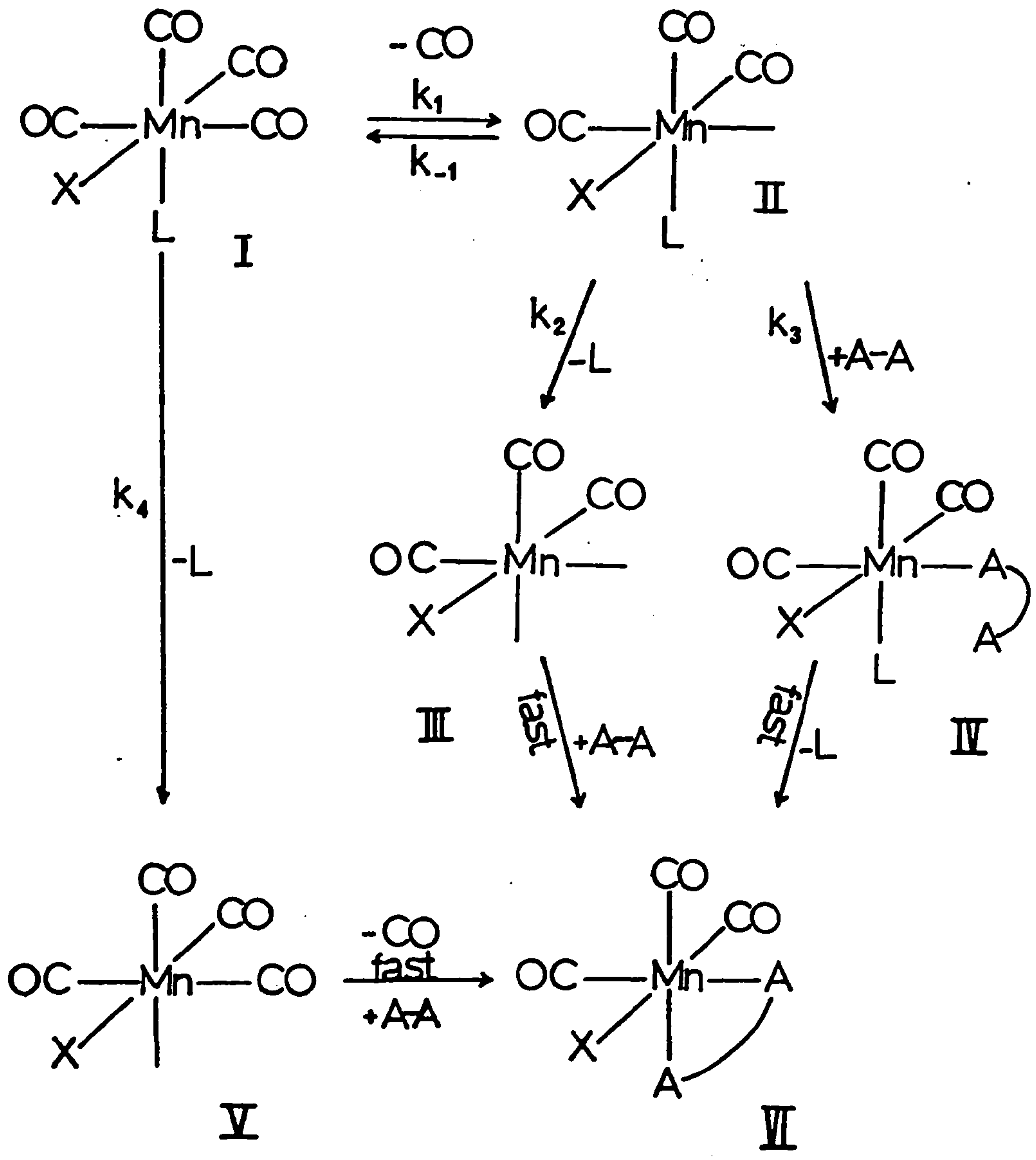

Figure 7.-Mechanism for the reaction of *cis*-Mn(CO)$_4$(PPh$_3$)Br with bidentates.

Assuming that k_{-1}[CO] is constant, we obtain

$$k_{obsd} = k' + k''[\text{A-A}]^{*} \tag{17}$$

In this mechanism the four and five-coordinated intermediates would presumably be solvated. The value of k_3[A-A] could be much smaller than k_{-1}[CO] if the bidentate encountered difficulties in approaching the coordination sphere of the central manganese atom.

2. If k_2 is negligible in comparison with k_3[A-A], and $k_3 << k_{-1}$[CO] as in the former situation, then

$$k_{obsd} = \frac{k_1 k_3[\text{A-A}]}{k_{-1}[\text{CO}]} + k_4 \tag{18}$$

Again, if k_{-1}[CO] is assumed to be constant, we have

$$k_{obsd} = k' + k''[\text{A-A}] \tag{19}$$

3. If k_4 is negligible in comparison with the other term on the right-hand-side of equation 15, and the same conditions as in mechanism(1) apply, then

$$k_{obsd} = \frac{k_1 k_2}{k_{-1}[\text{CO}]} + \frac{k_1 k_3[\text{A-A}]}{k_{-1}[\text{CO}]} \tag{20}$$

Therefore,

$$k_{obsd} = k' + k''[\text{A-A}] \tag{21}$$

The difference between mechanisms (1) and (3) would be the value of the intercept for the plot of k_{obsd} against [A-A]. In the case of mechanism (1) the intercept would be $(k_1k_2/k_{-1}[\text{CO}]) + k_4$, while for mechanism (3) it would be just $k_1k_2/k_{-1}[\text{CO}]$.

It was hoped that some light could be shed on the mechanism by measuring the rate of reaction of *cis*-$Mn(CO)_4(PPh_3)Br$ with CO. Unfortunately,

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[*] Throughout this chapter k' and k'' refer to combinations of a number of rate constants.

this reaction was very slow, and no rate constant was determined. Its value, however, is certainly much less than the intercept of the plot of k_{obsd} *vs.* [dipy], *i.e.* $k_4 < k_1k_2/k_1[CO]$.

If the conditions of mechanism (3) are imposed on mechanism (2), than equation 15 reduces to a purely second-order rate law, first-order in both substrate and bidentate.

4. One other possible mechanism must be considered for which there are three conditions. (a) k_4 is negligible with respect to the other term on the right-hand-side of equation 15 as in mechanism(3), (b) k_2 is negligible in comparison with k_3[A-A], and (c) k_{-1}[CO] is of comparable value to k_3[A-A]. Under these conditions we have

$$k_{obsd} = \frac{k_1k_3[A\text{-}A]}{k_{-1}[CO] + k_3[A\text{-}A]} \tag{22}$$

whence,

$$\frac{1}{k_{obsd}} = \frac{k_1[CO]}{k_1k_3[A\text{-}A]} + \frac{k_{-1}[CO]}{k_1} \tag{23}$$

The physical significance of this mechanism in comparison to the others is that in this case the rate at which the bidentate ligand attacks the reactive intermediate (II) is comparable to the rate of reformation of the starting material from the same intermediate. This alternative mechanism is particularly applicable to the reaction of *cis*-$Mn(CO)_4(PPh_3)Br$ with diarsine since the curvature in the plot of k_{obsd} *vs.* [diarsine] is mostly eliminated when $1/k_{obsd}$ is plotted against 1/[diarsine]. It would have been a very attractive proposition indeed if the intercepts of the plots of $1/k_{obsd}$ *vs.* 1/[A-A] for both diarsine and dipy were the same. This is what is predicted from equation 23, k_1 and k_{-1} being independent of the incoming ligand. However, no such agreement was found.

Thus, in the case of the reactions with dipy at least, the curvature in the plots of k_{obsd} *vs.* [dipy] are preferentially explained as arising from equation 15, where k_3[A-A] begins to have a value comparable to k_{-1}[CO].

In order to help explain the results obtained for the reactions of *cis*-$Mn(CO)_4(SbPh_3)Br$, the kinetics of its reaction with CO was investigated. The rate constant for this reaction at 40° in chloroform, was found to be 13×10^{-4} sec^{-1}, *i.e.* very close to the rate constant for the reaction of the same substrate with diphos and dipy. This may indicate that these reactions proceed *via* a slow dissociation of $SbPh_3$ followed by a fast addition of the bidentate. It is difficult to explain definitely the small difference between the rate of reaction of *cis*-$Mn(CO)_4(SbPh_3)Br$ with diarsine and with the other bidentates. Again, one may postulate that the mechanism for the former is the slow dissociation of a CO group followed by a fast addition of diarsine. That a combination of mechanisms involving the initial slow dissociation of both CO and $SbPh_3$ is taking place is also possible.

In conclusion, it is clear that although a number of possible mechanisms have been proposed, no *definite* mechanism(s) could be proposed to explain *all* the kinetic results available. The reactions which were studied are complex because two different ligands were being replaced by the entering bidentate. They present however, the interesting aspect of constituting only the second known example of second-order kinetics being observed for octahedral manganese carbonyl complexes.

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SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

PART I

1. The low-frequency infrared and Raman spectra of the complexes $Mn(CO)_5X$ (X=Cl,Br,I) in the solid state were recorded.
2. The solid-state infrared and Raman spectra of these complexes were also recorded in the CO stretching region and in the overtone and combination regions.
3. The CS_2 solution spectrum of $Mn(CO)_5I$ was recorded and compared to the solid-state spectrum.
4. A complete vibrational assignment was proposed for the complexes $Mn(CO)_5X$.
5. The solid-state infrared and Raman spectra of the complexes $[Mn(CO)_4X]_2$ (X=Br,I) were also measured.

PART II

A.

1. The exchange of ^{13}CO with the complexes <u>cis</u>-$Fe(CO)_4X_2$ (X=Br,I) was performed. All the fundamental CO modes and the ^{13}CO vibrations observed were assigned.
2. The force constants defining the CO stretching region were calculated.
3. By comparing the ratio of absorbances belonging to ^{13}CO groups <u>cis</u> or <u>trans</u> to the halogen it was found that the CO groups in the two positions exchanged at qualitatively equal rates.
4. The potential energy distributions were calculated and

related to the absolute intensities.

B.

1. The exchange of $C^{18}O$ with the complexes cis-$Mn(CO)_4LBr$ ($L=PPh_3,AsPh_3,SbPh_3$) was performed. All the fundamental CO modes and the isotopic vibrations were assigned.
2. The force constants defining the CO stretching region were calculated.
3. The rates of exchange of the different CO groups were compared qualitatively.
4. The complex cis-$Mn(CO)_4(SbPh_3)Br$ reacted with $C^{18}O$ to give, in part, $Mn(CO)_4(C^{18}O)Br$ in which the $C^{18}O$ was evident in both axial and radial positions indicating that an intramolecular rearrangement was taking place.

PART III

1. The reactions of $Mn(CO)_5X$ ($X=Cl,Br$) with monodentate phosphites were found to give novel compounds of the type cis-$Mn(CO)_2L_3X$.
2. The latter complexes reacted with diphos and triphos (A-A) to give cis-$Mn(CO)_2L(A\text{-}A)X$.
3. The complexes trans-$Mn(CO)_3[P(OPh)_3]_2X$ ($X=Cl,Br$) reacted with the bidentate ligands diphos, diars, diarsine, and dipy to yield two products, cis-$Mn(CO)_3(A\text{-}A)X$ and cis-$Mn(CO)_2L(A\text{-}A)X$. The products were separated by chromatography on alumina.
4. $Mn(CO)_5X$ reacted with triphos to give cis-$Mn(CO)_3(\text{triphos})X$ in which the ligand behaved as a bidentate. This complex reacted with another molecule of $Mn(CO)_5Br$ to give a

bridged complex $BrMn(CO)_3(triphos)Mn(CO)_4Br$.

5. The infrared spectra in the CO stretching region of all the new complexes prepared were recorded and the possible structures discussed.

PART IV

1. The thermal decomposition of the complexes trans-$Mn(CO)_3(PPh_3)_2X$ (X=Cl,Br,I) to give cis-$Mn(CO)_4(PPh_3)X$ was studied kinetically and found to follow a first-order rate law.
2. The reactions of the complexes cis-$Mn(CO)_4LBr$ ($L=PPh_3$, $AsPh_3$, $SbPh_3$) with the bidentate ligands diphos, diarsine, and dipy to give cis-$Mn(CO)_3(A-A)Br$ were also examined. The rates were found to depend both on the nature and on the concentration of the entering ligand. Possible mechanisms were suggested.

ERRATUM

bis(2-diphenylphosphino)phenylphosphine should be bis(2-diphenylphosphinoethyl)phenylphosphine in the LIST OF ABBREVIATIONS and on page 179